



Chemical weathering rates and atmospheric/soil CO₂ consumption of igneous and metamorphic rocks under tropical climate in southeastern Brazil



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ABSTRACT

Chemical weathering rates and atmosphere/soil CO₂ consumption of igneous and metamorphic rocks under tropical climate in southeastern Brazil were evaluated using the chemical composition of surface waters and fresh rocks and soil (horizon C) in the Upper Sorocaba River basin. Surface water samples were collected between June/2009 and June/2010, and analyses were performed to assess pH, electrical conductivity (EC), temperature and total dissolved solids (TDS), including Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, PO₄³⁻, NO₃⁻ and SiO₂. Fresh rocks and C horizon samples were also collected, taking into account their geological context, abundance and spatial density, to analyze major elements and mineralogy. The concentration of TDS and dissolved cations, anions and silica increased during the dry period in relation to the wet period, and the same behavior was observed for pH, EC and temperature. After corrections of anthropogenic contributions (ca. 21 t/km²/yr) and atmospheric inputs (ca. 19 t/km²/yr), the annual flux due to chemical weathering involving the igneous and metamorphic rocks was ca. 29 t/km²/yr. The CO₂ atmospheric/soil consumption in the Upper Sorocaba River basin was ca. 0.2 × 10⁶ mol/km²/yr, and when extrapolated to the entire Mantiqueira Orogenic Belt, accounted an estimated consumption of 0.07 × 10¹² mol/yr, representing 0.6% of the total CO₂ consumption flux derived from global average silicate weathering. The chemical weathering rates of igneous and metamorphic rocks in the Upper Sorocaba River basin were estimated at 15 m/My, respectively. The main weathering process in this watershed was the monossilicization, with partial hydrolyses of bedrock minerals, except quartz, which was not weathered and remained in the soil profile. The annual specific flux derived from igneous and metamorphic rocks at Upper Sorocaba River basin could be compared with watersheds in tropical climates. However, this value is higher than in other North American, European, Asian and African granitoid watersheds, and lower than in montane watersheds.

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1. Introduction

The determination of the chemical weathering and physical erosion is of interest to geoscientists, as this phenomenon provides the parameters needed for better soil exploration, in order to assist establishing agricultural fields and human settlements. Besides, the balance between these phenomena contributes to the geomorphological modeling of the Earth's surface. Chemical weathering of fresh rocks is the main mechanism of CO₂ consumption from the atmosphere and, consequently, has

the basic function of moderating the Earth's climate. The physical erosion is related to soil loss, acts on the weathered surface by removing the cover and carrying the particulate matter. In both processes, the dissolved and particulate materials are transported through rivers to the oceans, resulting in the deposition of Ca and Mg carbonates (and smaller amounts of Fe and Mn) and sediments, respectively.

The chemical weathering can be evaluated from the silica mass balance or from models using the dissolved sodium, calcium, potassium, magnesium and silica and total dissolved load concentrations, where inputs from rainfall require corrections (Amiotte-Suchet and Probst, 1993; Bain et al., 2001; Boeglin and Probst, 1998; Boeglin et al., 1997; Clow and Drever, 1996; Dessert et al., 2001; Dessert et al., 2003; Dupré et al., 2003; Edet et al., 2013; Gaillardet et al., 1997; Gaillardet

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et al., 1999; Gao et al., 2009; Gibbs, 1967; Grasby and Hutcheon, 2000; Gurumurthy et al., 2012; Johnson et al., 1968; Kattan et al., 1987; Land et al., 1999; Laraque et al., 2013; Li and Zhang, 2008; Li et al., 2014; Liu et al., 2016; Louvat, 1997; Louvat and Allègre, 1997, 1998; Louvat et al., 2008; Millot et al., 2002; Nkounkou and Probst, 1987; Oliva et al., 2003; Pacheco and Van der Weijden, 2002; Peray, 1998; Probst, 1986; Probst et al., 1994; Semhi et al., 2000; Stallard and Edmond, 1981, 1983, 1987; Tardy, 1968, 1969, 1971; Van der Weijden and Pacheco, 2006; Wang et al., 2016; White and Blum, 1995; Wu et al., 2013; Xu and Liu, 2010; Zakharova et al., 2007; Zhang et al., 2016).

The Earth's upper continental crust is constituted of ca. 25% for granitoid rocks, with their chemical weathering controlled mainly for temperature and runoff (Oliva et al., 2003). The Brazilian Southeast region is marked by the presence of Mantiqueira and Tocantins orogenic systems, where outcrops igneous and metamorphic rocks, and part of the São Francisco Craton (Fig. 1a). Due to their areal extent and the strong susceptibility to chemical weathering of these rocks under tropical climate, these areas play an important role in the global consumption of CO₂. Surprisingly, no chemical weathering rates have been proposed

for igneous and metamorphic rocks under tropical climate in these orogenic systems located in South America. Only few studies have focused on the chemical weathering rates of silicate rocks under different climates in Brazil, i.e. (a) equatorial climate: silicate rocks (igneous, metamorphic and sedimentary) in the giant Amazon River basin (Mortatti and Probst, 2003); (b) tropical climate: high grade metamorphic rocks of granulite facies in Bahia State (Moreira-Nordemann, 1980), Poços de Caldas alkaline rocks in Minas Gerais State (Bonotto et al., 2007) and sedimentary (mainly sandstones and mudstones - Conceição and Bonotto, 2003, 2004) and basalts (Conceição et al., 2015) rocks from Paraná Sedimentary basin in São Paulo State; (c) semi-arid climate: metamorphic (gneiss, amphibolite and quartzite) in Bahia State (Moreira-Nordemann, 1984).

A study involving a mass-balance in a large basin would allow to estimate the dissolved material flux of the Mantiqueira and Tocantins Orogenic Belts, characterizing and quantifying the respective chemical weathering rates and atmospheric/soil CO₂ consumed during the water-rock/soil interaction process. However, this research would be very complex because of the different types of rocks, climate, soil

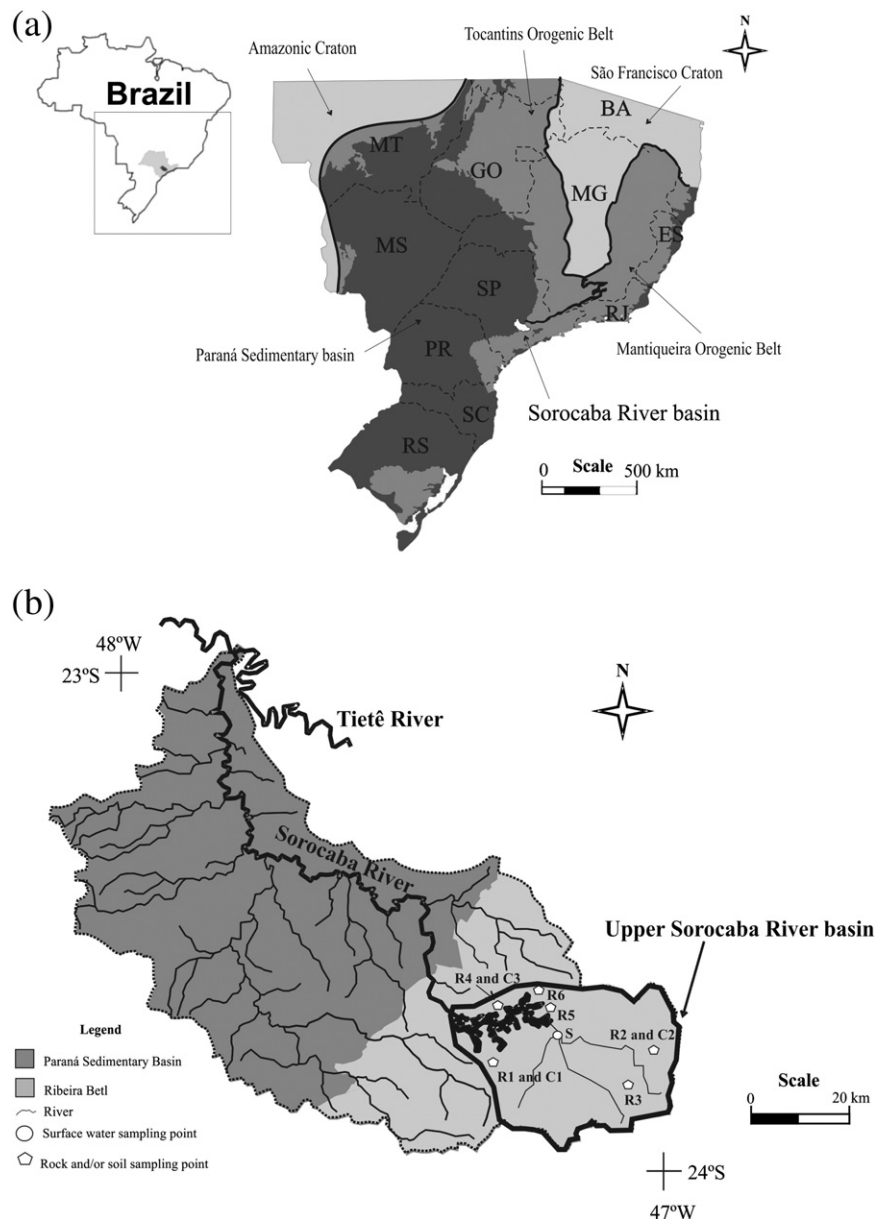


Fig. 1. Map of eastern South America showing the main geological units relative to the Cratons, Orogenic Belts and Paraná Sedimentary Basin (a) (Modified from Hasui, 2010). The upper Sorocaba River basin with location of the sampling points (b). R1, R2, R3, R4, R5 and R6 = fresh rocks; C1, C2 and C3 = soil (horizon C); S = surface water.

thickness, reliefs and human activities in every region of this great basin. Studies of chemical weathering and atmospheric/soil CO₂ consumption in small watersheds, with one single type of rock, allow understanding the control parameters these processes and show that chemical dynamics in these areas can be applied globally (Millot et al., 2002). Thus, a small watershed could be chosen to assess the current chemical weathering rates and atmospheric/soil CO₂ consumption of igneous and metamorphic rocks under tropical climate in Brazil.

In this context, the Upper Sorocaba River basin, located in the eastern part of São Paulo State, Brazil, is an ideal study area to assess the chemical weathering rates and atmospheric/soil CO₂ consumption of igneous and metamorphic rocks under tropical climate from the Ribeira Belt, which is composed for metamorphic rocks of the Embu Complex and the São Roque Group, with their associated granites (Fig. 1b). Also, the influences of rainwater and human activities on the annual flux of elements or compounds transported by the Upper Sorocaba River were explained. In addition, after these necessary corrections, the main chemical weathering processes and associated CO₂ flux were modeled using the weathering index defined by Tardy (1971) and the mass balance between fluvial and pluvial transport of Ca, Mg, K and Na, respectively. Thus, our results provide new insight into the chemical weathering and atmospheric/soil CO₂ consumption of granitoid rocks in South America, which can be used to complement global knowledge about the water-rock interaction process in granitoid watersheds under different climates conditions in future studies.

2. Overview of the Upper Sorocaba River basin

The Upper Sorocaba River basin occupies an area of 929 km², between latitudes 23°35'02" and 23°45'37" S and longitudes 46°57'29" and 47°21'00" W (Fig. 1b), with a total population of 110,577 inhabitants. The Sorocaba River is formed by the Una, Sorocabuçu and Sorocamirim rivers, and its headwaters are located in the Ibiúna, Cotia, Vargem Grande Paulista and São Roque municipalities. The land use in this watershed are mostly related to intense agricultural activities based on irrigation and use of agrochemicals (393 km²), forest (256 km²), fields (147 km²), urban areas (71 km²), small farms and recreation areas (35 km²) and an important reservoir called Itupararanga (27 km²). The Itupararanga Reservoir is used for recreation and water supply to >700,000 people in the Sorocaba and Votorantim cities, and it is responsible for regularizing the Sorocaba River discharge (IPT, 2006).

According to IPT (2006), the Upper Sorocaba River basin climate is tropical with hot and humid in summer and dry in the winter, and an average annual temperature of 18 to 22 °C. The monthly and annual mean historical rainfall data between 1960 and 2004 was obtained from the Brazilian Company of Aluminum (CBA, 2006), which has a

weather station installed near the dam spillway of the Itupararanga Reservoir. The average annual rainfall was 1492.7 mm, with January the wettest (average of 248 mm) and August the driest months (average of 43 mm) (Fig. 2a). The wettest year during the analyzed historical period was in 1983 (2540 mm) and 1963 was the driest year (969 mm). The highest value of rainfall in 1983 was primarily associated with the occurrence of the El Niño phenomenon, and consequent increase annual precipitation rates.

The monthly and annual affluent discharge data for Itupararanga Reservoir for this same period were also provided by CBA (2006), and the data showed that 50% of the time the inflow to the reservoir was approximately 13 m³/s, being 1983 and 1969 the years with the highest and lowest average affluent discharge (35.5 and 5.3 m³/s), respectively. February was the month with the highest average affluent discharge (21.7 m³/s), while the lowest average was in September (7.0 m³/s) (Fig. 2a). The average monthly discharge for the same period showed a significant positive linear correlation with rainfall (Fig. 2b).

The study area is located in the Mantiqueira Orogenic Belt, formed during the Proterozoic-Paleozoic, divided into the Araçuaí, Ribeira and Tijuca Belts (Hasui, 2010). The current geological setting of this region is associated with convergence events, with closing of oceans and continental and microcontinental collisions, called Brasiliano Cycle, which was divided into here phases: Brasiliano I (900–700 Myr), Brasiliano II (670–530 Myr) and Brasiliano III (580–490 Myr) (Campanha et al., 2008; Cordani et al., 2002; Hasui, 2010; Heilbron and Machado, 2003; Janasi et al., 2001; Laux et al., 2005; Pimentel et al., 2004a, 2004b; Piuçana et al., 2003a, 2003b; Seer et al., 2005; Silva et al., 2005a, 2005b; Silva et al., 2002a, 2002b, 2002c; Valeriano et al., 2004).

Geologically, the Upper Sorocaba Basin consists of several geological structures related to the Ribeira Belt, emphasizing the São Roque and Embu Domains, outcropping at 6% and 23% of the study area, respectively, with associated granites with both complexes (71% of the study basin area) (IPT, 2006). The São Roque Domain has metamorphic rocks of the São Roque Group (phyllites - Godoy et al., 1996a, 1996b) and associated granitoid complexes, such as São Francisco granite (syenogranites and monzogranites - Godoy, 1989; Godoy and Figueiredo, 1991; Hackspacher et al., 1991) and São Roque granite (diorites e granodiorites - Arraes, 2006). The gneisses and migmatites of the Embú Complex predominate in the Embú Domain (Godoy et al., 1996b), with the occurrence of Ibiúna (monzogranites and syenogranites - Arraes, 2006) and Caucaia granites (monzogranites and syenogranites - Arraes, 2006; Godoy et al., 1996a). Recent sediments constitute the valley bottom deposits that occur along the Una, Sorocabuçu and Sorocamirim rivers (Godoy, 1989).

The Upper Sorocaba River is included in the Atlantic Plateaus Geomorphologic Province (Ross, 1996; Ross and Moroz, 1997). The dominant relief forms in this unit comprises hills with shapes of convex

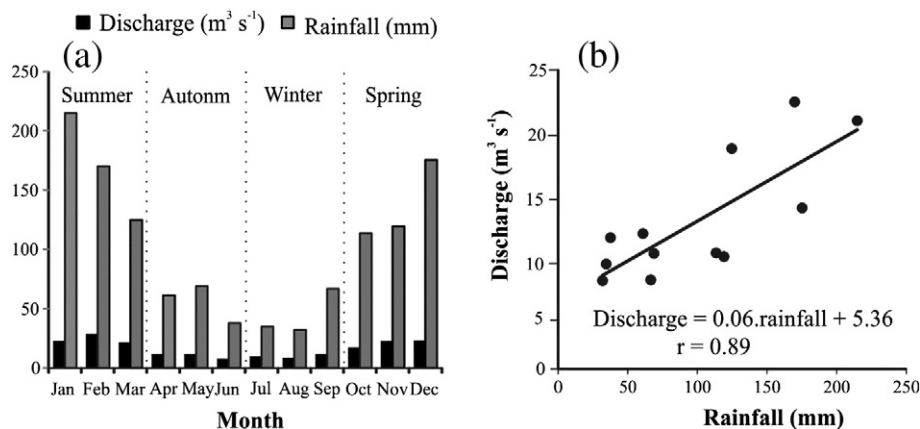


Fig. 2. Monthly average rainfall for a 44-year period (1960–2004) in the upper Sorocaba River basin (CBA, 2006) (a). Relationship between average rainfall and discharge for the same period (b).

tops and deep valleys, with altitudes between 800 and 1000 m and slope above 20%. The predominant soils in this watershed are Oxisols, Ultisols and Inceptisols, according to USDA (1999) nomenclature, corresponding to Red–Yellow Latosol (51%), Red–Yellow Argissol (42%) and Cambisols (7%) in the Brazilian soil classification (EMBRAPA, 2013; Oliveira et al., 1999). The original vegetation that covered the Upper Sorocaba River basin soils was characterized by forests, brushwood, fields, savannas and lowland vegetation. However, most of the vegetation along this basin has been removed for agricultural occupation and urbanization processes (IPT, 2006).

3. Sampling and analytical methods

The surface water samples from the Upper Sorocaba River basin were collected in one sampling point (23°38'07" S and 47°13'23" W) for hydrochemical analyses on Jun/17, Jul/21, Aug/25, Sep/22, Nov/10 and Dec/12 in 2009 and Jan/20, Feb/23, Mar/30, Apr/27, May/27 and Jun/24 in 2010 (S in Fig. 1b). Located upstream of the Itupararanga Reservoir, this sampling point drains an area of 680 km², in order to prevent the possible influences of this reservoir on the chemical species quantified. These dates were selected because they cover the extremes of the rainfall regime (see Fig. 2a, the minimum values are recorded in July–August and the annual maximum occurs in January–February). This is consequently reflected in the discharge regime of the Upper Sorocaba River, as demonstrated in Fig. 2b. The discharge was estimated according to the float method by Eq. (1):

$$Q = \frac{A \cdot D \cdot C}{T} \quad (1)$$

where Q is the discharge (m³/s), A is the cross-section of the river (m²), D is the distance to estimate the water velocity in the river (m), C is the empirical coefficient (0.9) and T is the time the floating body will take to travel the distance D (s).

The dissolved chemical species concentrations were determined from 1000 mL of river water composite samples, collected in the left and right margins and in the main axis of the river current at a 1.5 m depth using a single stage punctual sampler (Mortatti, 1995). The composite samples were stored in identified polyethylene bottles and kept at 4 °C until chemical analyses processing. The physicochemical parameters (pH, temperature and electrical conductivity - EC) were measured in the field using portable equipments. The pH was determined using a Digimed DM2 pH meter, with a relative accuracy of 0.01% and calibrated with standard solutions DM-S1B (pH 4.01) and DM-S1A (pH 6.86). The electrical conductivity and temperature were measured using the Digimed DM3 sensor, with a resolution of 0.01 μS/cm, relative accuracy of 0.05% and automatic temperature compensation, calibrated with conductivity standard conductivity solutions (DM-S6 A for 1412 μS/cm) and DM-S6B (146.9 μS/cm).

The fluvial water samples (300 mL) were filtered through cellulose membrane filters (0.45 μm) and sent for analysis of dissolved cations, anions and silica. Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, PO₄³⁻ and NO₃⁻ were quantified by ion chromatography using Dionex ICS-90 equipped with IonPac® CS12A 4 × 250 mm Analytical and IonPac® AS14A 4 × 250 mm Analytical columns, which presented detection and quantification limits of 0.001 mg/L and 0.01 mg/L, respectively (Dionex Corporation, 2004; Ribani et al., 2004). The HCO₃⁻ was represented by the alkalinity content and was quantified by Gran method (Edmond, 1970). The Si⁴⁺ was quantified using Inductively Coupled Plasma–Optical Emission Spectrometry, ICP-OES Optima 3000 DV, with a detection limit of 0.020 mg/L and the result was expressed in terms of SiO₂. The total dissolved solids (TDS) correspond to the sum of cations, anions and silica.

Representative rock samples (R1, R2, R3, R4, R5 and R6 in Fig. 1b) were collected throughout the basin, taking into account their geological context, abundance and spatial representativeness. Soil samples

(C1, C2 and C3 in Fig. 1b) were collected in horizon C at the same sites as the rock samples. All rock and soil (horizon C) samples were analyzed for SiO₂, Al₂O₃, Fe₂O₃, TiO₂, K₂O, Na₂O, MgO, MnO, CaO, P₂O₅ and LOI (loss on ignition at 1000 °C) by X-ray fluorescence (XRF – Phillips PW 2510). All details on quality control (accuracy and precision) and detection limits are presented in Nardy et al. (1997). The identification of minerals was performed by X-ray diffractometry (XRD – Siemens D5000) on powdered samples, using a wide angle X-ray diffractometer, operating at 40 kV and 40 mA, with CuKα radiation.

4. Results

4.1. Chemistry of the upper Sorocaba River

Table 1 reports the physical and chemical parameters of all surface waters sampled from the Upper Sorocaba River. In this work, the wet and dry periods are from October to March and from April to September, respectively. The weighted average element/compound concentration was calculated by the following equation:

$$C_{RE} = \frac{\sum_{i=1}^n C_i \cdot Q_i}{\sum_{i=1}^n Q_i} \quad (2)$$

where C_{RE} is the weighted average element/compound concentration (mg/L), C_i is the element concentration for the i th measurement (mg/L) and Q_i is the discharge of the river in the day of the i th measurement (m³/s).

As expected, the highest discharge value was obtained in the rainy season (57.24 m³/s) and the lowest in the dry season (5.79 m³/s), with an average discharge rate during the sampling period of 22.86 m³/s. The Upper Sorocaba River waters were slightly acidic, with average pH of 6.4, ranging from 6.3 to 6.7. The water temperature variation followed the seasons, with the lowest and highest values in the dry (14.2 °C) and rainy (24.3 °C) seasons, respectively, with intermediate values in autumn and spring. The average electrical conductivity was 76.1 μS/cm with significant seasonal variability, with minimum values (57.9 μS/cm) characterized during the rainy season due to the dilution effect by the discharge increase, and maximum values in the dry season (90.7 μS/cm).

With regard to dissolved cations, anions and silica, the concentration of all elements/compounds increased during the dry period in relation to the wet period. Table 1 indicates that Ca²⁺ and HCO₃⁻ were the most abundant cation and anion in surface waters, with a weighted average presenting the following trend (in mg/L): Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ > + and HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻ > PO₄³⁻, respectively. For all samples, the charge balance was lower than 10%, with an anionic deficit in most of the samples analyzed (Fig. 3a), assuming an ionic equilibrium for natural waters (Probst, 1992). The absence of these charges can be attributed to the anionic presence of dissolved organic carbon (DOC) that were not compiled in this study, such as DOC concentrations of 5.35 μeq per mg of carbon (Drever, 1997). This fact was also reported for other drainage basins, such as in African rivers, Niger (Boeglin and Probst, 1996), Congo and Ubangui (Probst et al., 1992b), as well as in the Amazon River – Brazil (Tardy et al., 2005) and in Asian rivers (Gurumurthy et al., 2012; Wu et al., 2013).

The total dissolved solids (TDS) values obtained at the Upper Sorocaba River increased from wet to dry periods. The TDS concentration along the study period was influenced by rainfall, presenting a dilution effect during the rainy season, as illustrated in Fig. 3b. The instantaneous daily flux can be evaluated from the TDS concentration in the Upper Sorocaba River and its daily discharge. These parameters are a function of discharge, in accordance with most world rivers (Berner and Berner, 1996), with the majority of the TDS load transported during the wet

Table 1
Physical and chemical parameters for the Upper Sorocaba surface waters.

Parameter	Units	Date of sampling											C_{RE}^a	
		06/17/09	07/21/09	08/25/09	09/22/09	11/10/09	12/12/09	01/20/10	02/23/10	03/30/10	04/27/10	05/27/10		06/24/10
Discharge	m^3/s	5.79	6.76	19.20	15.54	26.51	56.75	57.24	28.71	23.59	16.76	10.91	6.52	22.86
pH		6.5	6.7	6.5	6.5	6.3	6.4	6.5	6.4	6.5	6.5	6.6	6.7	6.4
Temperature	$^{\circ}C$	14.3	14.2	14.9	16.6	23.2	22.8	24.3	22.7	24.0	22.9	19.1	17.3	19.7
EC ^b	$\mu S/cm$	90.0	90.7	71.3	85.0	71.6	64.8	57.9	87.8	72.0	72.9	74.9	74.8	76.1
Na ⁺	mg/L	11.55	10.54	6.90	7.32	6.80	5.80	6.06	6.46	7.16	6.69	8.62	8.14	6.76
Ca ²⁺	mg/L	11.00	10.00	7.10	8.00	7.00	6.18	6.20	8.20	9.22	9.01	8.00	9.10	7.41
K ⁺	mg/L	1.95	2.09	1.50	1.66	1.53	1.41	1.35	1.70	1.80	1.90	2.10	2.07	1.59
Mg ²⁺	mg/L	1.70	1.61	1.40	1.50	1.30	1.34	1.35	1.40	1.60	1.65	1.75	1.76	1.44
SiO ₂	mg/L	15.00	12.00	10.03	10.54	8.95	7.23	6.70	9.17	8.08	8.63	9.08	10.16	8.46
SO ₄ ²⁻	mg/L	2.14	2.26	1.62	1.04	0.89	0.95	0.93	0.75	1.26	1.43	0.95	1.32	1.09
NO ₃ ⁻	mg/L	2.59	1.11	0.45	0.80	0.15	0.07	0.10	0.17	0.86	1.78	1.89	2.71	0.55
Cl ⁻	mg/L	14.79	12.71	8.65	7.74	7.30	5.98	6.11	8.09	9.37	10.75	11.42	10.98	7.90
HCO ₃ ⁻	mg/L	47.00	40.00	26.00	32.00	29.69	25.40	26.50	31.00	30.56	31.66	34.00	42.00	29.43
PO ₄ ³⁻	mg/L	0.09	0.04	0.03	0.06	0.04	0.04	0.02	0.05	0.05	0.05	0.16	0.17	0.05
TDS ^c	mg/L	107.80	91.82	63.67	70.64	63.64	54.39	55.33	66.99	69.96	73.54	77.95	88.41	64.67

^a Weighted average element/compound concentration.

^b Electrical conductivity.

^c Total dissolved solids.

period (Fig. 3c). Using the weighted average of the TDS concentration (64.67 mg/L), the mean discharge at this sampling point (22.86 m^3/s) and the area (680 km^2), it was possible to calculate the total amount of dissolved material removed annually, which was ca. 69 t/(km^2/yr).

4.2. Rocks and soils (C horizon)

The Embu Complex (migmatitic gneisses rocks - R2) is composed for biotite ($K(Mg,Fe)_3(Si_3Al)O_{10}(OH)_2$), muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$) and sillimanite (Al_2SiO_5), quartz (SiO_2), microcline ($KAlSi_3O_8$) and oligoclase ($(Na,Ca)(Si,Al)_4O_8$). The presence of quartz veins associated is common. The São Roque Group rocks (metarhytmities - R6) presented quartz, muscovite and biotite. Sample R1 (Ibiúna granite - Fig. 4a) is a monzogranite comprised of quartz, microcline and oligoclase, biotite and hornblende ($Ca_2Na(Mg,Fe)_4(Al,Fe,Ti)AlSi_8AlO_{22}(OH)_2$). Sample R3 (Caucaia granite - Fig. 4b) is an inequigranular syenogranite, consisting primarily of quartz, microcline, oligoclase and biotite. Sample R4 was collected in the São Francisco granite (Fig. 4c), considered an equigranular syenogranite, presented quartz, microcline, oligoclase and biotite. Sample R5 (São Roque granite - Fig. 4d) is an inequigranular monzogranite with microcline megacrystals, quartz, oligoclase, biotite and hornblende. Overall, the average mineralogical composition of the granites is 35% microcline, 23% oligoclase, 30% quartz, 10% biotite and 2% hornblende.

Table 2 shows the chemical composition of igneous and metamorphic rocks from the Upper Sorocaba River basin. The element concentrations in the rocks depend on their genesis and the geological context of the region. The granites silica content ranged from 66.57 to 74.75 wt%,

with an average of 71.15 wt%, characterizing the rocks in relation to its natural composition as acid rocks ($SiO_2 > 65\%$). The diagrams from Peacock (1931) and Irvine and Baragar (1971), presented in Fig. 4e and f, indicate that the granites are calcic and subalkaline rocks. In relation to tectonic environment (Fig. 4g and h), the granites can be classified as orogenic granitoids, i.e. island arc granitoids (IAG) or continental arc granitoids (CAG) or continental collision granitoids (CCG). The C horizons are depleted in Na^+ , K^+ , Ca^{2+} and Mg^{2+} and enriched in Fe_2O_3 , Al_2O_3 and TiO_2 in relation to igneous and metamorphic rocks. The main minerals in these soils are quartz, kaolinite ($Al_2Si_2O_5(OH)_4$), goethite ($FeOOH$), rutile (TiO_2), gibbsite ($Al(OH)_3$) and a small amount of unweathered microcline, oligoclase and biotite.

5. Discussion

5.1. Sources of major ions

White and Blum (1995) modified the mass-balance technique proposed by Garrels and MacKenzie (1967) to measure the chemical weathering of rocks in the watershed, which can be described as:

$$F_w = \frac{F_{river} - F_{wetfall} - F_{dryfall} \pm F_{ion} \pm F_{bio} - F_{anthr}}{S} \quad (3)$$

where F_w is the natural flux due to chemical weathering ($t/km^2/yr$), F_{river} is the measured river flux (t/yr), $F_{wetfall}$ and $F_{dryfall}$ are the atmospheric inputs (t/yr), F_{ion} is the dissolved solids from ion exchange sites in

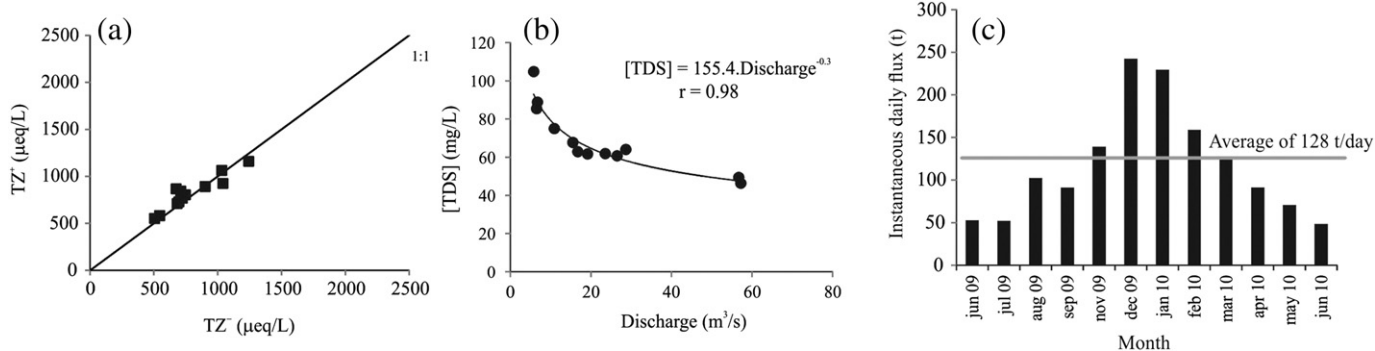


Fig. 3. Charge balance in the upper Sorocaba River basin, with TZ^+ and TZ^- corresponding to total dissolved cations and anions, respectively (a). Relationship between discharge vs. [TDS] in the upper Sorocaba River basin (b). Instantaneous daily flux of TDS in the upper Sorocaba River basin (c).

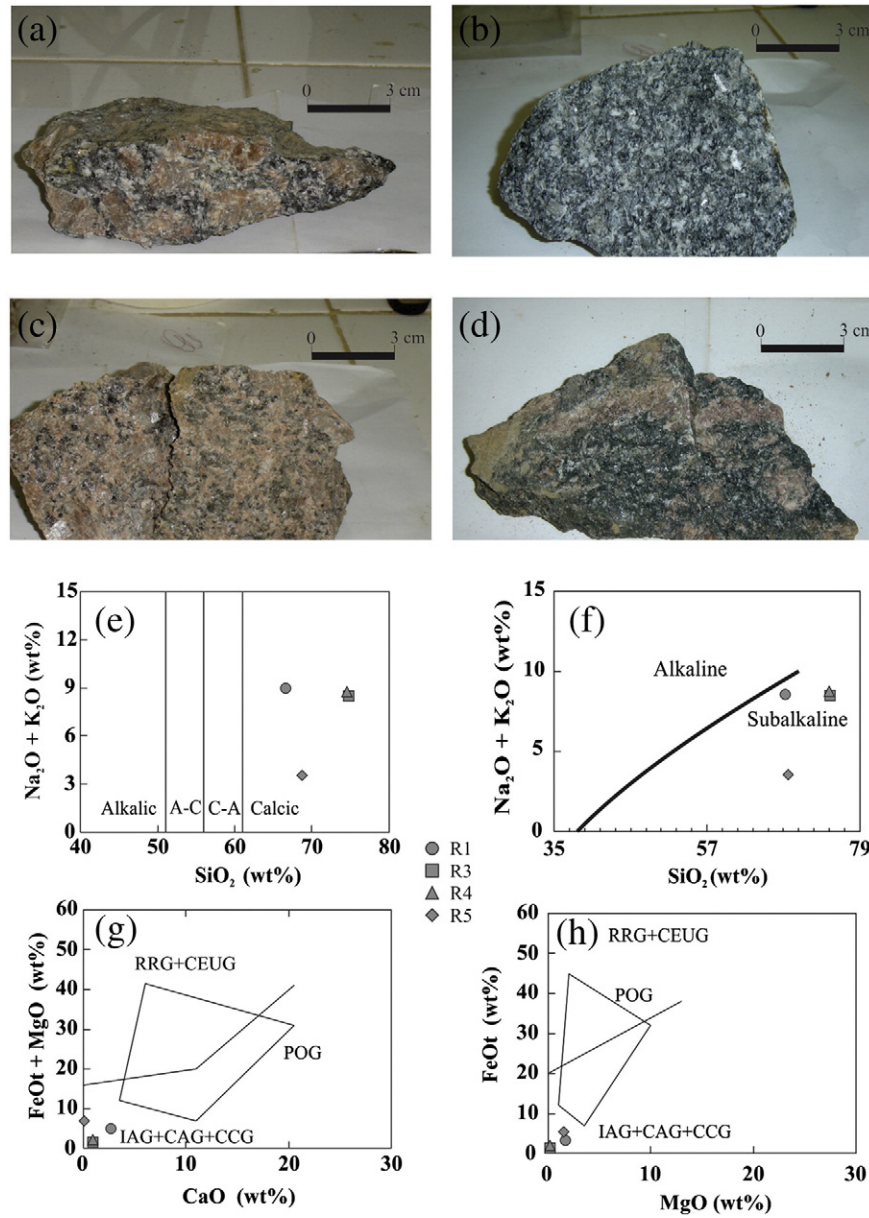


Fig. 4. Granites samples collected in the upper Sorocaba River basin: Ibiúna (a), Caucaia (b), São Francisco (c) and São Roque (d). Diagrams from Peacock (1931) (e), Irvine and Baragar (1971) (f) and Maniar and Piccoli (1989) (g and h). IAG - island arc granitoids, CAG - continental arc granitoids, CCG - continental collision granitoids (CCG), POG - postorogenic granitoids, RRG - rift-related granitoids, CEUG - continental epeirogenic uplift granitoids and OP oceanic plagiogranites (OP).

clay minerals (t/yr), F_{bio} is the dissolved solids due to changes in biomass (t/yr), F_{anthr} is the anthropogenic inputs (t/yr) and S is the watershed area (km^2).

The net flux from exchange processes in the Upper Sorocaba River basin may be considerably less substantial than the removal of Na^+ , K^+ , Ca^{2+} and Mg^{2+} by possible weathering reactions occurring in the

Table 2
Chemical composition (wt%) of fresh rocks and soil (horizon C) from the Upper Sorocaba River basin.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI ^a
<i>Fresh rock</i>											
R1	66.57	0.61	15.15	3.63	0.06	1.68	2.65	3.71	5.27	0.25	0.43
R2	52.54	1.20	25.10	9.48	0.01	0.34	0.30	0.38	5.30	0.05	5.61
R3	74.75	0.13	13.49	1.53	0.05	0.13	0.93	3.56	4.95	0.04	0.47
R4	74.54	0.19	12.40	2.18	0.06	0.15	0.88	3.44	5.35	0.05	0.77
R5	69.72	0.71	13.56	5.96	0.03	1.47	1.10	4.13	3.45	0.16	0.72
R6	68.73	0.94	16.69	6.66	0.26	0.44	0.08	0.11	3.65	0.15	2.30
<i>Soil (horizon C)</i>											
C1	65.07	0.88	16.44	6.01	0.07	0.17	0.06	0.19	3.15	0.04	7.40
C2	50.48	1.51	26.49	7.98	0.03	0.14	0.04	0.09	2.97	0.16	9.40
C3	67.89	0.63	16.95	5.38	0.03	0.18	0.02	0.02	1.16	0.04	7.10

^a Loss on ignition.

basin. Grasby and Hutcheon (2000) suggest that if the net biomass in a basin remains relatively constant through time, then the change in biomass flux should be minimal. Thus, the Eq. (3) can be reduced to Eq. (4), which only considered the anthropogenic inputs (mainly originating from domestic sewage and industrial and agricultural activities) and atmospheric influences in the mass balance.

$$F_w = \frac{F_{river} - F_{wetfall} - F_{dryfall} - F_{anthr}}{S} \quad (4)$$

The flux of dissolved cations, anions, silica and TDS in the Upper Sorocaba River (F_{river}) was calculated using the weighted average element/compound concentration (Table 1), the mean discharge at this sampling point (22.86 m³/s) and the area (680 km²).

5.1.1. Atmospheric inputs

Many human activities are significant sources of element/compounds emissions to the atmosphere, which have important influence in the chemical weathering rates. São Paulo State is considered potentially problematic area due to the intense industrial activities. The annual flux of dissolved chemical species in the Upper Sorocaba basin due to atmospheric inputs was studied by Conceição et al. (2011), which indicated that the pH varied from 5.5 to 6.8, being Ca²⁺ the main ion responsible for controlling the rainwater pH, with the ionic concentrations decreased in the following order: Ca²⁺ > Na⁺ > Mg²⁺ > K⁺ for cations and SO₄²⁻ > HCO₃⁻ > NO₃⁻ > Cl⁻ > PO₄³⁻ for anions. Besides the annual atmospheric deposition appeared to be controlled mostly by following sources: mining activities and cement factories (Ca²⁺ and HCO₃⁻), natural soil dust (Na⁺, Mg²⁺ and HCO₃⁻), fossil fuel burning (SO₄²⁻) and agriculture activities (K⁺, NO₃⁻ and PO₄³⁻). To correct the atmospheric inputs ($F_{wetfall}$ and $F_{dryfall}$), it was used the annual atmospheric flux of dissolved cations and anions and TDS in the Upper Sorocaba River basin obtained by Conceição et al. (2011).

5.1.2. Anthropogenic influences

Sardinha et al. (2008) evaluated the annual flux of cations and anions at Upper Sorocaba River basin, indicating how anthropogenic influences are affecting these values. The results indicated that the absence of treatment of domestic waste at Ibiúna city and the strong agricultural activities reduced the water quality upstream from the Ituparanga Reservoir. At the same study, it was proposed corrections due to anthropogenic influences considering a mass balance equation that takes into account the Sorocaba River before its entry into Ituparanga Reservoir and also its tributaries (Una, Sorocamirim, and Sorocabuçu rivers), which indicated an anthropogenic influence in the dissolved cations and anions concentrations of 35% of Ca²⁺, 23% of Mg²⁺, 65% of Na⁺, 10% of K⁺, 14% of HCO₃⁻, 53% of SO₄²⁻, 36% of NO₃⁻, 91% of Cl⁻ and 54% of PO₄³⁻ (Sardinha et al., 2008). According to Mortatti et al. (2008) and Mortatti et al. (2012), the silica concentration in the sewage can be despised. Using both information and the F_{river} of dissolved cations, anions, silica and TDS values, the anthropogenic influences (F_{anthr}) were calculated.

5.1.3. Contributions of different sources

According to the geological map (Fig. 1b), only silicate rocks are described in the Upper Sorocaba River basin. Table 3 presents the values of F_{river} , $F_{wetfall}$ and $F_{dryfall}$ and F_{anthr} and, consequently, the natural flux due to chemical weathering of igneous and metamorphic rocks (F_w) obtained by using Eq. (4). The contributions from different sources (in %) are illustrated in Fig. 5. Only SO₄²⁻, NO₃⁻, Cl⁻ and PO₄³⁻ yielded negative values, whereas a positive mass-balance was found for the other element/compounds, i.e. 1.15 t/km²/yr of Na⁺, 1.56 t/km²/yr of Ca²⁺, 0.83 t/km²/yr of Mg²⁺, 1.02 t/km²/yr of K⁺, 8.96 t/km²/yr of SiO₂, 21.39 t/km²/yr of HCO₃⁻ and 28.54 t/km²/yr of TDS. After the corrections for atmospheric and anthropogenic inputs in the watershed, the chemical weathering reactions of the igneous and metamorphic rocks, anthropogenic inputs and atmospheric inputs represent ca. 29 t/km²/yr (42%), 21 t/km²/yr (30%) and 19 t/km²/yr (28%), respectively, of the total dissolved load (ca. 69 t/km²/yr) carried out of the Upper Sorocaba River basin (Table 3). The local bedrock influence in the chemical weathering is also observed for the relation between Ca²⁺/Na⁺ vs. Mg²⁺/Na⁺ (Fig. 6a) and Ca²⁺/Na⁺ vs. HCO₃⁻/Na⁺ (Fig. 6b), with all samples presenting more similarity of silicate end member (Gaillardet et al., 1999).

5.2. Chemical weathering processes

The R_E index (Eq. (5)) proposed by Tardy (1971) was used to determine the chemical weathering process of igneous and metamorphic rocks in the Upper Sorocaba River basin, assuming the R_E index is equal to the molecular ratio SiO₂/Al₂O₃ of the neoformation of secondary minerals in the soil profile, and modified by Boeglin and Probst (1998). The weathering process can be characterized according to the classification of Pedro (1966): for R_E = 0, only aluminum and iron are fixed as insoluble hydroxides, a process known as complete hydrolysis or alitization; when R_E = 2, the weathering process is called partial hydrolysis with monossialitization, with kaolinite stability domain; for R_E = 4, the predominant mechanism is the partial hydrolysis with bisialitization, producing montmorillonite minerals type.

$$R_E = \frac{3 \cdot F_K + 3 \cdot F_{Na} + 2 \cdot F_{Ca} + 1.25 \cdot F_{Mg} - F_{SiO_2}}{0.5 \cdot F_K + 0.5 \cdot F_{Na} + F_{Ca} + 0.75 \cdot F_{Mg}} \quad (5)$$

where F_K , F_{Na} , F_{Ca} , F_{Mg} and F_{SiO_2} are the annual flux of dissolved potassium, sodium, calcium, magnesium and silica, respectively, after necessary corrections (in mol/yr).

The igneous and metamorphic rocks had an R_E value of 2.2, with the predominance of monossialitization, confirmed by the presence of kaolinite in the C horizon. This chemical weathering process can also be confirmed using the diagram proposed by Nesbitt and Young (1984, 1989) shown in Fig. 7, i.e. the occurrence of a partial hydrolysis of bedrock minerals, with some of the SiO₂ remaining in the profile and Na⁺, Ca²⁺, K⁺ and Mg²⁺ were removed. Thus, Na⁺ may be released by the hydrolysis of oligoclase and hornblende, Ca²⁺ by the hydrolysis of oligoclase and hornblende, Mg²⁺ by the hydrolysis of biotite and hornblende and K⁺ by the hydrolysis of microcline, biotite and muscovite. In addition, the Upper Sorocaba River basin does not contain volumetrically significant Cl⁻, NO₃⁻, PO₄³⁻ or SO₄²⁻ bearing minerals. Therefore, only small inputs of these anions into the rivers due to water-rock

Table 3

The annual flux (t/km²/yr) of dissolved cations, anions and silica and TDS in the Upper Sorocaba River basin.

Species	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	SiO ₂	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	HCO ₃ ⁻	PO ₄ ³⁻	TDS ²
F_{river}	7.18	7.86	1.53	1.69	8.96	1.16	0.58	8.37	31.19	0.05	68.57
$F_{wetfall} + F_{dryfall}^a$	1.36	3.55	0.35	0.50	—	4.55	2.11	1.17	5.44	0.22	19.25
F_{anthr}	4.67	2.75	0.35	0.17	—	0.61	0.21	7.62	4.37	0.03	20.78
F_w	1.15	1.56	0.83	1.02	8.96	-4.01	-1.74	-0.42	21.39	-0.20	28.54

^a Conceição et al. (2011).

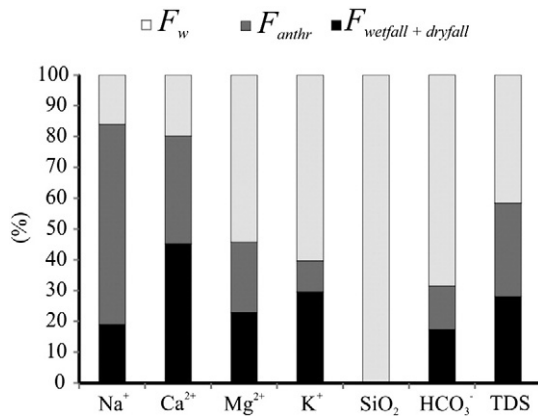


Fig. 5. Contribution of different sources (%) to dissolved cations, SiO₂, HCO₃⁻ and TDS in the Upper Sorocaba River. F_w = natural flux due to chemical weathering, F_{anthr} = anthropogenic, $F_{wetfall}$ and $F_{dryfall}$ are the atmospheric inputs.

interactions are expected. Quartz and a small amount of microcline, oligoclase and biotite are not weathered and remain in the soil profile.

5.3. Atmospheric/soil CO₂ consumption

The chemical weathering process of rocks in a drainage basin involves the carbonic acid reacting with primary minerals of rocks, producing dissolved inorganic carbon, mainly HCO₃⁻, as previously reported in the literature (Boeglin and Probst, 1998; Gurumurthy et al., 2012; Lasaga et al., 1994; Meybeck, 1987; Mortatti and Probst, 2003; Probst, 1992; Probst et al., 1994; Stallard and Edmond, 1981, 1983, 1987). The chemical reactions, hydrolysis of silicates and dissolution of carbonates, are closely related to the production of HCO₃⁻. The total HCO₃⁻ produced during the silicate weathering comes from atmospheric/soil CO₂, while for the carbonates alteration only 50% of HCO₃⁻ produced come from atmospheric/soil CO₂, and the other half comes from the own carbonate dissolution (Boeglin and Probst, 1998). The lithology of the Upper Sorocaba River basin is related to silicate rocks,

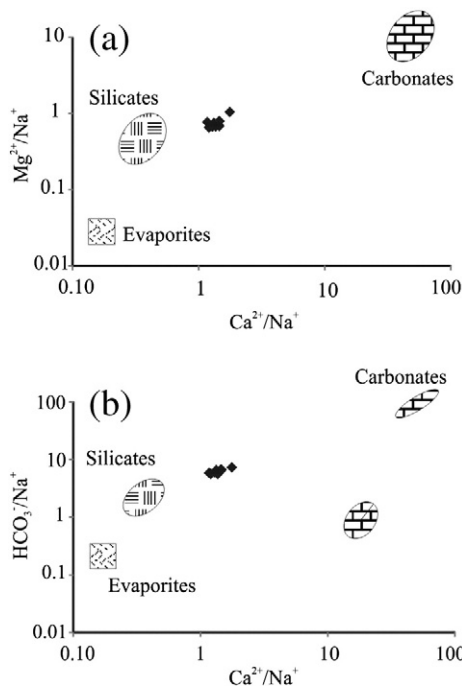


Fig. 6. The Na-normalized molar ratios diagrams in the dissolved phase of the Upper Sorocaba River. The end member reservoirs represent the small watershed with single lithology (carbonates, silicates and evaporites, according to Gaillardet et al. (1999)).

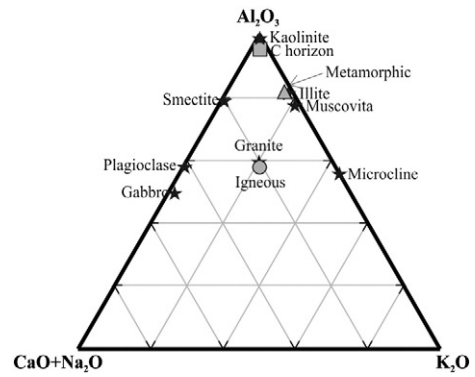


Fig. 7. (Na₂O + CaO)-Al₂O₃-K₂O diagram showing the weathering trends (Nesbitt and Young, 1984, 1989) in the Upper Sorocaba River basin. Igneous, metamorphic and C horizon corresponding to average composition of the 4 granites, 2 metamorphic rock and 3 soil samples, respectively.

which allows calculating the atmospheric/soil CO₂ consumption rate by the sum of cation flux from the weathering process of these rocks, according to Eq. (6) (Gaillardet et al., 1999). In Eq. (6), the coefficients (1 or 2) are derived from stoichiometric coefficients of weathering reactions (Mortatti and Probst, 2003).

$$FCO_2 = F_{Na} sil + F_K sil + 2F_{Mg} sil + 2F_{Ca} sil \quad (6)$$

where FCO_2 is the total atmospheric/soil CO₂ due to chemical weathering (in mol/yr) and $F_{Na} sil$, $F_K sil$, $F_{Mg} sil$ and $F_{Ca} sil$ are the annual flux of sodium, potassium, magnesium and calcium, respectively, due to silicate weathering (in mol/yr).

The atmospheric/soil CO₂ consumed during the chemical weathering of igneous and metamorphic rocks was ca. 0.2×10^6 mol/km²/yr. This value is higher than the world continental average (0.161×10^6 mol/km²/yr) and the silicate rocks average (0.034×10^6 mol/km²/yr) (Meybeck, 1987). However, it is lower than in carbonate areas (0.800×10^6 mol/km²/yr) (Meybeck, 1987), in silicate rocks from the Amazon basin (0.331×10^6 mol/km²/yr) (Mortatti and Probst, 2003) and basaltic watersheds worldwide, i.e. in the São Miguel island - Azores (0.6×10^6 mol/km²/yr - Louvat and Allègre, 1998), in the Iceland (0.7×10^6 mol/km²/yr - Louvat, 1997), in the Decan Traps (1.3×10^6 mol/km²/yr - Dessert et al., 2001), in Réunion Island (2.3×10^6 mol/km²/yr - Louvat and Allègre, 1997), in Java (6.4×10^6 mol/km²/yr - Louvat, 1997) and Paraná continental flood basalts (0.4×10^6 mol/km²/yr - Conceição et al., 2015).

The map of eastern South America that illustrates the main geological units of the Cratons, Orogenic Belts and Phanerozoic basins (Fig. 1a), allows to obtain the surface area of ca. 350,000 km² for the Mantiqueira Orogenic Belt. Thus, the annual atmospheric/soil CO₂ consumed during chemical weathering of the igneous and metamorphic rocks can be extrapolated to the entire Mantiqueira Orogenic Belt, and it is estimated as 0.07×10^{12} mol/yr. This value represents 0.6% of the total CO₂ consumption flux derived from global average silicate weathering (Gaillardet et al., 1999).

5.4. Chemical weathering rate

The use of mass balance models based on the concentration of TDS, ions Na⁺, K⁺, Mg²⁺ and Ca²⁺ and dissolved silica should assume that all silicate minerals are transformed into kaolinite during the water-rock interaction process. However, as discussed earlier, during the chemical weathering of igneous and metamorphic rocks in the Upper Sorocaba River basin, the quartz in the saprolite remains unaltered, indicating its low solubility when compared to other silicate minerals. Therefore, the mass balance conducted should be reviewed in light of the current chemical weathering processes in the Upper Sorocaba

River basin. **Boeglin and Probst (1998)** proposed a mass-balance model to measure the chemical weathering rate (W_{Ch}) in granitoid watersheds, considering the fresh rock composition and the proportion between kaolinite and residual quartz on the saprolite composition, as described in Eq. (7).

$$W_{Ch} = \frac{F_{SiO_2} \cdot [P_q(d_q - d_k) + 100 \cdot d_q]}{S_0 [P_q(d_q - d_k) + 100 \cdot d_q] - 10d_k \cdot d_q \cdot [(100 - P_{SiO_2}) \cdot P_q + 100P_{SiO_2}]} \quad (7)$$

where F_{SiO_2} is the annual flux of silica (t/km²/yr), P_q is the residual quartz content in saprolite (%), d_k is the density of kaolinite (1.45 t/m³), d_q is the density of quartz (2.65 t/m³), S_0 is the silica content in the parent rock (t/m³) and P_{SiO_2} is the silica content in kaolinite (= 46.5%).

The residual quartz (P_q) in saprolite can be calculated using Eq. (8), where Q_0 and D_R are the quartz content in bedrock (kg/m³) and the original quartz dissolution rate (in %), respectively. The validity of this mass-balance model depends on the bedrock chemical weathering into saprolite is isovolumetric (1), all primary silicate minerals are fully transformed in kaolinite, with the exception of quartz (2), all silica transported by the surface waters comes from the silicate mineral hydrolyses, occurring at the bottom of the weathering profile (3) and the flux of silica exported by surface water is conservative (4) (**Boeglin and Probst, 1998**).

$$P_q = \frac{100 \cdot d_q Q_0 (100 - D_R)}{[d_k \cdot d_q \cdot 10^5 + Q_0 (100 - D_R) (d_q - d_k)]} \quad (8)$$

The annual flux of dissolved silica in the river waters after atmospheric corrections (F_{SiO_2}) was 8.9 t/km²/yr or 8900 kg/km²/yr (**Table 3**). Three major bedrock types were found in the Upper Sorocaba River basin: granites, gneisses and metarhytmities, which occupy 71, 23 and 6% of the total watershed area, respectively. Considering these areas and the chemical composition of the bedrocks (**Table 2**) in the Upper Sorocaba River basin, the weighted average silica content was 66.89 wt%. Using a density of 2.65 t/m³ or 2650 kg/m³ related to bedrocks, the amount of silica (S_0) is 1772 kg/m³. Considering an average of 30% as amount of quartz in bedrock, a value of 795 kg/m³ can be obtained for Q_0 . Besides, taking a quartz dissolution rate of 15% (D_R), as indicated by **Tardy (1969)**, the quartz residual (P_q) content in saprolite corresponded to 38.5%.

Using Eq. (7), the chemical weathering rate of 15 m/Myr were estimated for igneous and metamorphic rocks in the Upper Sorocaba River basin, respectively. The value found in this study is lower than those calculated for diorites from Puerto Rico (58 m/Myr) (**White et al., 1998**) and carbonates from the Seine River basin, France (25 m/Myr) (**Roy et al., 1999**). However, this value is higher than that evaluated for crystalline rocks (8.5 m/Myr) from the Congo Basin (**Probst, 1992**) and ultramafic schist (8 m/Myr) from the Yaou catchment in French Guyana (**Freyssinet and Farah, 2000**). The Niger River basin, which consists primarily of granite and schist, and the temperate Brubaker basin dominated by metamorphic rocks (Pennsylvania, USA), also have lower chemical weathering rates (4.7–6.1 m/Myr - **Boeglin and Probst, 1998**; and 5.5 m/Myr - **Price et al., 2008**, respectively) than the Upper Sorocaba River basin.

In Brazil, there are few studies on the current chemical weathering of rocks, including the average chemical weathering rate of ca. 15 m/Myr obtained for silicate rocks (igneous, metamorphic and sedimentary) in the Amazon River basin (**Mortatti and Probst, 2003**). **Moreira-Nordemann (1980)** determined a chemical weathering rate of 40 m/Myr for metamorphic rocks in the Preto River basin, Bahia State. **Bonotto et al. (2007)** quantified a chemical weathering rate of 15 m/Myr for alkaline rocks from Poços de Caldas, Minas Gerais State. For sedimentary (mainly sandstones and mudstones) and basalts rocks from Paraná Sedimentary basin in São Paulo State were estimated a chemical

weathering rate of 22 m/Myr (**Conceição and Bonotto, 2003**) and 6 m/Myr (**Conceição et al., 2015**), respectively.

5.5. Comparing the annual flux due to chemical weathering with other watersheds

The key factor in chemical weathering rates is the fresh rock composition (mineral constituents, texture and structure), where evaporites and carbonates weather more easily than silicate rocks (**Garrels and Mackenzie, 1971**; **Meybeck, 1987**). The weathering rate of 67.8 t/km²/yr in the Bow River carbonate basin in southern Alberta, Canada (**Grasby and Hutcheon, 2000**), confirmed that carbonate rocks, since in cold climates, weather more easily than the igneous and metamorphic rocks in the Upper Sorocaba River basin. In general, basalts weather much faster than granitoid rocks, being the weathering of basalts an important contribution to the total flux of dissolved material carried to the ocean (**Dessert et al., 2001**; **Dupré et al., 2003**). This hypothesis is confirmed when the result of this study is compared with basaltic watersheds, i.e. Deccan Traps - 37 t/km²/yr (**Dessert et al., 2001**), São Miguel - 35 t/km²/yr (**Louvat and Allègre, 1998**), Iceland - 36 t/km²/yr (**Louvat et al., 2008**), Réunion Island - 102 t/km²/yr (**Louvat and Allègre, 1997**), Java - 326 t/km²/yr (**Louvat et al., 2008**) and Paraná flood basalts - 30 t/km²/yr (**Conceição et al., 2015**). The temperature and runoff are the main parameters controlling the chemical weathering of basaltic watersheds (**Dessert et al., 2001**).

The relationship between the annual flux of granitic rocks and climatic conditions was defined by **White and Blum (1995)**, in a study of 68 small watersheds composed of crystalline rocks. The annual flux of two granitic provinces in Canada were evaluated by **Millot et al. (2002)**, which proposed that the temperature and runoff act positively on granitic weathering rates. **Oliva et al. (2003)** used the database of a small watershed located in granitic environments, including the **White and Blum (1995)** database plus additional data taken from the literature published, and they also concluded that the temperature and runoff are the main parameters controlling the chemical weathering in granitic watersheds. However, according to **West et al. (2005)**, any single parameter cannot control the silicate weathering rates, which require consideration in multiple dimensions.

To compare the annual flux due to chemical weathering of igneous and metamorphic rocks in different granitic watershed, the procedure proposed by **Millot et al. (2002)** will be used, which considered only the specific annual flux of Na⁺, K⁺, Ca²⁺ and Mg²⁺, excluding the silica and anions from the weathering estimated. Thus, the annual specific flux derived from igneous and metamorphic rocks at Upper Sorocaba River basin is ca. 4.6 t/km²/yr. **Fig. 8** presents the relationship between annual flux versus temperature and runoff for granitoid watersheds. A large range for the annual flux can be observed, from those of the Karelia region - NW Russia (ca. 0.3 t/km²/yr - **Zakharova et al., 2007**) to those of the West Southern Alps (ca. 98 t/km²/yr - **Jacobson and Blum, 2003**). A strong and positive linear correlation between annual flux and runoff is observed, as already reported for a similar log-log correlation between annual flux and runoff in small watersheds or in large rivers of the world (**Bluth and Kump, 1994**; **Dunne, 1978**; **Gaillardet et al., 1999**; **Millot et al., 2002**). According to **Gaillardet et al. (1999)**, this log-log correlation had made little physical sense, and that the intensity of annual flux increases to counterbalance the dilution.

The chemical weathering rate obtained in this work presents the same order of magnitude of watersheds in warmer and humid tropical climates, such as the igneous and metamorphic rocks located in Puerto Rico, Guayana Shield in South America and Malaysia. The annual flux obtained for Upper Sorocaba River basin is higher than in other North American, European and Asian igneous and metamorphic watersheds characterized by colder weather. In montane watersheds is possible to verify higher values of chemical weathering rates due to elevated runoff, even in cold climate condition. In some African regions with tropical climate have similar annual flux to the watersheds located in cold and

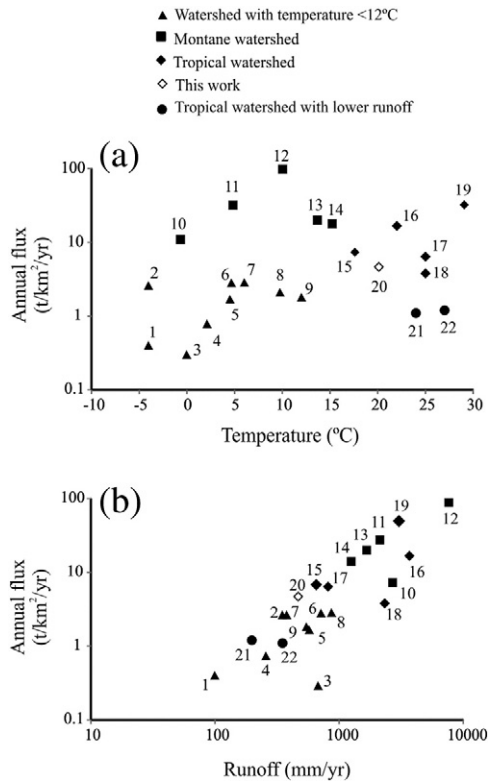


Fig. 8. Relationship between the annual flux vs. the temperature of the air (a) and the annual runoff values (b) for granitoid watersheds. 1 - Slave and 5 - Grenville provinces - Canada (Millot et al., 2002), 2 - Norway–Russia border area (Koptsik et al., 1999), 3 - Karelia region - NW Russia (Zakharova et al., 2007), 4 - Siberia (Huh and Edmond, 1999), 6 - USA and 8 - Appalachians (White and Blum, 1995), 7 - Scotland (Bain et al., 2001), 9 - France (Meybeck, 1986), 10 - Swiss Alps (Hosein et al., 2004), 11 - High Himalaya and 14 - Lesser Himalaya (West et al., 2002), 12 - East Southern Alps and 13 - West Southern Alps (Jacobson and Blum, 2003), 15 - South-eastern China (Wu et al., 2013), 16 - Puerto Rico (McDowell and Asbury, 1994), 17 - Malaysia (Vegas-Vilarrubia et al., 1994), 18 - Guayana Shield (Edmond et al., 1995), 19 - South-western India (Gurumurthy et al., 2012), 20 - this study, 21 - rivers Nyong - Cameroon (Viers et al., 2000) and 22 - Niger (Boeglin and Probst, 1998).

drier climates, such as the basins of the river Niger and Nyong (Cameroon). Although both areas have high rainfall and temperature, these factors do not control the annual flux due to chemical weathering of igneous and metamorphic rocks, but rather other local factors such as soil thickness, high water residence time in the soil and vegetation, besides the lateritic cover preventing significant percolating water and fresh rocks interaction (Boeglin and Probst, 1998; Viers et al., 2000). Thus, both temperature and runoff are the main factors related to chemical weathering of igneous and metamorphic rocks (e.g. White and Blum, 1995; Millot et al., 2002), but other factors also must be considered to explain the water/rock interactions in granitoid watersheds such as relief, soil cover and water time residence in the soil profile (Oliva et al., 2003; West et al., 2005).

6. Conclusion

This study explains the chemical weathering rate and atmosphere/soil CO₂ consumption of igneous and metamorphic rocks under tropical climate in southeastern Brazil. The concentration of dissolved cations, anions and silica increased during the dry period in relation to the wet period. The same behavior is observed for pH, electrical conductivity, temperature and TDS. The most abundant cations and anions in surface waters were Ca²⁺ and HCO₃⁻, with a weighted average presenting the following trend (in mg/L): Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ and HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻ > PO₄³⁻, respectively. The metamorphic rocks of the Embu Complex and São Roque Group presented a predominance of

quartz, muscovite and biotite, whereas igneous rocks, represented by granites, had a mineralogical composition of quartz, microcline, oligoclase and biotite. The main minerals in the C horizons (soils) were quartz, kaolinite, goethite, rutile and gibbsite, and these soils are depleted in Na⁺, K⁺, Ca²⁺ and Mg²⁺ and enriched in Fe₂O₃, Al₂O₃ and TiO₂ in relation to bedrocks. After corrections of anthropogenic contributions (ca. 21 t/km²/yr) and atmospheric inputs (ca. 19 t/km²/yr), the annual flux due to chemical weathering of igneous and metamorphic rocks was ca. 29 t/km²/yr, representing 42% of the total dissolved load carried out of the Upper Sorocaba River basin (ca. 69 t/km²/yr). The main weathering process in this watershed is the monossialitization, confirmed by the presence of kaolinite in the C horizon, with the primary quartz remains in the soil profile. The atmospheric/soil CO₂ consumed during the chemical weathering was ca. 0.2 × 10⁶ mol/km²/yr, with a chemical weathering rate estimated at 15 m/Myr. Our results confirm that carbonates and basalts weather much faster than igneous and metamorphic rocks found in the Upper Sorocaba River basin. Besides, the annual specific flux derived from igneous and metamorphic rocks at Upper Sorocaba River basin is in the same order of magnitude of watersheds in warmer and humid tropical climates. However, this annual flux is higher than in other North American, European, Asian and African igneous and metamorphic watersheds, and lower than in montane watersheds, reinforced a climate control associated with other factors to explain the water/rock interactions in granitoid watersheds. This study associated with future researches in granitoid watersheds under different climates conditions (equatorial, subtropical and semi-arid) in Brazil or in South America should be used to complement global knowledge about the water-rock interaction process.

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