Hydrochemistry applied to assess the chemical weathering and soil removal rates in the Sorocaba River basin, São Paulo State

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ABSTRACT: Chemical weathering and soil removal rates are responsible for the Earth's landscape, composition of surface and groundwater, producing the soils and buffering the composition of the atmosphere. This study aimed to assess the chemical weathering and soil removal rates in the Sorocaba River basin, São Paulo State, Brazil, allowing answering the questions about the dynamics of fluvial transport of dissolved and suspended solids, the chemical weathering processes and associated atmospheric/soil CO2 consumption, and the relationship between chemical weathering and soil erosion rates. The annual specific flux of total suspended solids and total dissolved solids were 49.59 and 60.97 t/km²/yr. The chemical weathering process dominant in the Sorocaba River basin was the monosiallitization (RE = 2.4), with an associated atmospheric/soil CO2 consumption of 2.3 × 10⁵ mol/km²/yr. The chemical weathering and soil removal rates were 7.2 and 29.8 m/Myr, respectively, indicating a soil thickness reduction. Finally, the soil removal rate in the Sorocaba River basin is almost 3-fold higher than the Cenozoic soil removal rates, being this difference related to the current land use which increased the soil removal processes.

KEYWORDS: Fluvial geochemistry; disturbed watershed; water-rock interactions; rainwater and anthropogenic influences.

INTRODUCTION

Chemical weathering is typically a destructive process, which allows the development of new minerals from the weathering of primary minerals. In addition, water-rock interactions are responsible for the Earth's landscape, composition of surface and groundwater, producing the soils and buffering the composition of the atmosphere, being this process one of the main mechanisms of atmospheric CO2 removal and consequent deposition of carbonates Ca²⁺ and Mg²⁺ in oceans, playing an important role in moderating terrestrial climate (Gaillardet et al. 1999, Millot et al. 2002). Residual products are subject to other processes of the supergene cycle, such as erosion, transport, and sedimentation, which ultimately lead to continental denudation, with consequent flattening on the relief (Teixeira et al. 2000).

Pioneering studies to investigate the nature and composition of the dissolved and suspended load transported by rivers were performed in the 1960-70s (Barth 1961, Johnson et al. 1968, Gibbs 1970, Tardy 1971, Martin and Meybeck 1979). Since then, many studies have been carried out to assess chemical weathering and soil erosion rates using mass-balance models adjusted to atmospheric and anthropogenic (mainly originating from domestic sewage and industrial and agricultural activities) contributions, once the total river fluxes integrate the contributions of these different sources (Probst 1986, 1992, Meybeck 1987, Lasaga et al. 1994, White and Blum 1995, Boeglin and Probst 1996, 1998, Boeglin et al. 1997, Gaillardet et al. 1999, Semhi et al. 2000, Millot et al. 2002, Meybeck et al. 2003, Walling and Fang 2003, Riebe et al. 2004, Chakrapani 2005, Weijden and Pacheco 2006, Louvat et al. 2008, Gurumurthy et al. 2012, Laraque et al. 2013, Li et al. 2014). The interest in assessing the chemical weathering and soil removal rates in watersheds under different geological and climatic setting also occurred in Brazil (Stallard and Edmond 1981, 1983, 1987, Moreira-Nordemann 1980, 1984, Mortatti et al. 1997, 2008, Gaillardet et al. 1997, Bortoletto Junior et al. 2002, Conceição and Bonotto 2003, 2004, Mortatti and Probst 2003, Bonotto et al. 2007, Sardinha et al. 2010, Fernandes et al. 2012, 2016a, Conceição et al. 2015, Couto Júnior et al. 2019, Spatti Júnior et al. 2019).

The state of São Paulo established 21 units of Water Resources Management (UGRHI), according to Law No. 7,663, published in December 30th, 1991 (São Paulo 1991). The Sorocaba River basin belongs to UGRHI-10 (Médio Tiête — Sorocaba), presents well-defined climatic seasonality (tropical climate) and a diverse geological and geomorphological context. Successive cycles of development and diversification of human activities have occurred since its occupation in the seventeenth century. Nowadays, this watershed covers 18 municipalities (1,212,376 inhabitants), an important industrial park, with over 1,850 enterprises and...
large agricultural areas (IBGE 2010). Approximately 65% of the demands for public supply in the Sorocaba River basin are supplied by Itupararanga Reservoir (IPT 2006). Despite its importance, few studies have been conducted in the Sorocaba River basin related to the rainwater chemical composition and annual atmospheric deposition (Conceição et al. 2011, 2013), the chemical weathering rates in the Upper Sorocaba River basin (Sardinha et al. 2010, Fernandes et al. 2016a), the water quality of the Itupararanga Reservoir (Pedrazzi et al. 2013, 2014), and the origin and flux of trace elements and isotopic composition of particulate organic matter in suspended sediment (Fernandes et al. 2012, 2016b).

Thus, this study aims to assess the chemical weathering and soil removal rates in the Sorocaba River basin, allowing answering the following questions:

• What are the dynamics of fluvial transport of dissolved and suspended solids?
• What are the chemical weathering processes and associated atmospheric/soil CO₂ consumption?
• What is the relationship between the chemical weathering and soil removal rates?

STUDY AREA

The Sorocaba River basin is located in the southeastern portion of São Paulo State, Brazil, between latitudes 23 and 24°S and longitudes 47 and 48°W, and occupies an area of 5,269 km². Considered the most important tributary of the left bank of Tietê River, Sorocaba River travels 227 km before flowing into Tiete River, in Laranjal Paulista municipality (IPT 2006). This watershed is inserted into two main geomorphological units: Atlantic Plateau and Paulista Peripheral Depression (Ross 1996 — Fig. 1). The Atlantic Plateau presents metamorphic rocks belonging to the São Roque Group and Embu Complex, with associated granitic rocks (Godoy et al. 1996). The relief is comprised of hills shapes with convex tops and deep valleys with altitudes that range between 800 and 1,000 m a.s.l. and slope above 20% (Ross 1996, Perrota et al. 2005). In the Paulista Peripheral Depression outcrop the sedimentary rocks belonging to the Parana Sedimentary Basin (Paleozoic-Mesozoic), i.e., Itararé Group (diamictic, sandstones, mudstones, and rhythmites), Guatá Group (siltstones and sandstones), and Passa Dois Group (siltstones, mudstones, and shales) (Conceição and Bonotto 2004, IPT 2006). The relief presents hills with tabular and large convex tops, prevailing altitudes between 600 and 700 m a.s.l. and slopes ranging from 5 to 10% (Ross 1996, Perrota et al. 2005).

The predominant soils in the study area are Red Argisol (49%), Red Latosol (38%), and Red-Yellow Latosol (9%), according to the Brazilian soil classification (EMBRAPA 2013, Oliveira et al. 1999), corresponding to Ultisols and Oxisols in the USDA nomenclature (USDA 1999), respectively. Forests, fields, and Savanna characterized the original vegetation. Currently, with the agricultural occupation and the urbanization processes, land use is characterized by the predominance of the

Figure 1. Geological map of Sorocaba River basin with location of the fluvial sampling point at the Tatui municipality, and the pluviometric and fluviometric stations (E4-019 and 4E-004, respectively).
pastures and fields (77%), followed by areas with agricultural crops (14%), reforestation areas (3%), original vegetation cover (2%), and urban areas (4%) (IPT 2006).

The climate is Cwa type, according to the Köppen classification (Köppen 1948), characterized by the predominance of rainfall in summer and dryness in winter, with an average annual temperature of 18 to 22°C (IPT 2006). Figure 2A shows the monthly averages of rainfall and discharge in the Sorocaba River basin from 1979 to 2008, calculated from the monthly historical data of the Pluviometric station E4-019 (23º20’S, 47º41’W) and the Fluviometric station 4E-004 (23º19’S, 47º46’W) (DAEE 2010), respectively. During this period, the average annual rainfall was 1,276 mm, where January and August were the months with the highest and lowest rainfall values (236 and 35 mm, respectively). In the same historical period, the average annual discharge was 53.8 m³/s, with the highest monthly average in February (98.3 m³/s) and lowest in August (33.7 m³/s). Figure 2B shows a significant positive linear correlation between the average monthly values of rainfall and discharge for these 30 years.

MATERIALS AND METHODS

Sampling and analytical methods

The river sampling point was established approximately 500 m upstream from the confluence of the Sorocaba and Tatuí rivers, in the municipality of Tatuí (Lat. 23º19’09”S, Long. 47º46’44”W), as can be seen in Figure 1, covering an area of 3,942 km², i.e., 74.8% of the total area of the Sorocaba River basin, with a total population of 1,061,023 inhabitants (IBGE 2010) and the urban sewage treatment percentage estimated at 17.5% (IPT 2006). This sampling point was chosen due to there being a fluviometric station installed (limnigraphic ruler and an automatic limnigraph), managed by DAEE/CTH, with daily discharge data since 1940. These data were used to validate the discharge measurements performed during the sampling period.

Twelve fluvial water sample collections were carried out at the Sorocaba River, covering one complete hydrological cycle (Jun/2009 to Jun/2010). Sorocaba River waters (1,000 mL) were collected in each sampling at 1.5 m deep, using a single-stage punctual sampler. The samples were separated into two 500 mL aliquots, one crude and the other preserved with 0.1 mL of concentrated H₂SO₄. Both aliquots were stored in identified polyethylene bottles and kept at 4°C until laboratory processing.

Discharge (Q), hydrogenionic potential (pH), electrical conductivity (EC), and temperature (T) were characterized in the field using direct reading equipment. The discharge was represented by the product of the wet river channel cross-section area (m²), obtained by bathymetry, and the average velocity of the water flow in this section (m/s) quantified using a Digital Micromolinetes Global Water FP 101. The pH values were determined using a DM2 Digimed portable pHmeter, with a relative accuracy of 0.01% and calibrated with standard solutions DM-S1B (pH 4.01) and DM-S1A (pH 6.86). In addition, EC and T were quantified using the Digimed DM3 sensor, with a resolution of 0.01 mS/cm, relative accuracy of 0.05% and automatic temperature compensation, previously calibrated with conductivity standard solutions DM S6A (1,412 mS/cm and DM S6B (146.9 mS/cm).

Crude fluvial water samples were filtered through cellulose membrane filters (0.45 mm), previously dried and weighed. These filtered samples were analyzed by ion chromatography Dionex ICS-90 equipped with analytical columns IonPac® CS12A 4x250 mm and IonPac® AS14A 4x250 mm, for the quantification of dissolved ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, PO₄³⁻, and NO₃⁻), with a detection limit of 0.001 mg/L (Dionex Corporation 2004) and quantification limit of 0.01 mg/L (Ribani et al. 2004). The HCO₃⁻ was represented by the alkalinity content and was quantified by the Gran method (Edmond 1970). The preserved fluvial water samples were filtered through a glass fiber membrane filter (0.3–0.6 mm) and used in the quantification of dissolved Si⁴⁺ concentration by optical emission spectrometry with inductively coupled argon plasma, ICP-OES Optima 3000 DV, with a detection limit of 0.02 mg/L, and the result was expressed in terms of SiO₂. The total dissolved solids (TDS) correspond to the sum of dissolved cations, anions and silica. The total suspended solids (TSS) was quantified by gravimetry (APHA 1999), considering the retained material in the cellulose membrane filter after drying in a stove at

Figure 2. (A) Monthly average rainfall and discharge for a 30-year period (1979–2008) in the Sorocaba River basin, and (B) relationship between the monthly average rainfall and discharge for the same period.
60°C to constant weight. The analysis of the river water samples was performed at Stable Isotope Laboratory (dissolved ions, HCO₃⁻ and TSS) and Analytical Chemistry Laboratory (dissolved silica), both located at CENA/USP.

**Theoretical background**

The fluvial fluxes (F₇ᵣᵢᵥₑ in t/km²/yr) of dissolved chemical species, TDS and TSS related to chemical weathering and soil removal processes, were calculated using a mass balance model expressed in Equation 1 (White and Blum 1995), considering negligible the fluxes from the biomass change and derived from the ionic exchange sites in clay minerals.

\[ F_{w} = F_{\text{river}} - F_{\text{rainfall}} - F_{\text{anthropogenic}} \]  \hspace{1cm} (1)

In which:

- \( F_{\text{river}} \) = the measured river flux (t/km²/yr);
- \( F_{\text{rainfall}} \) = the atmospheric inputs (t/km²/yr);
- \( F_{\text{anthropogenic}} \) = the anthropogenic influences (t/km²/yr).

The \( R_{E} \) index can be used to determine the predominant process of chemical weathering of rocks in a drainage basin. Initially proposed by Tarby (1971), this index is equivalent to the molecular ratio (SiO₂)/(Al₂O₃) of secondary minerals neoformation within the soil profile. Boeglin and Probst (1998) modified the \( R_{E} \) index, being expressed by the molar ratio of chemical dissolved species in the surface waters (Eq. 2).

\[ R_{E} = \frac{3K + 3Na + 2Ca + 1.25Mg}{0.5K + 0.5Na + Ca + 0.75Mg} \]  \hspace{1cm} (2)

The atmospheric/soil CO₂ consumption during chemical weathering processes (\( F_{\text{CO}_2} \) in mol/km²/yr) was estimated by the sum of corrected fluxes of Na⁺, K⁺, Ca²⁺, and Mg²⁺ (\( F_{\text{ion}} \)) according to Equation 3 (Gaillardet et al. 1999, Gurumurthy et al. 2012).

\[ F_{\text{CO}_2} = F_{\text{Na}} + F_{\text{K}} + 2F_{\text{Ca}} + 2F_{\text{Mg}} \]  \hspace{1cm} (3)

The chemical weathering of rocks (\( IQ \)) – in t/km²/yr can be estimated through the sum of the corrected annual fluvial fluxes of Na⁺, K⁺, Ca²⁺, Mg²⁺, and SiO₂ (\( F_{\text{w}}(\text{ion}) \) - in t/km²/yr), i.e., after correction of atmospheric inputs and anthropogenic contributions, according to Equation 5 (Probst 1992). The ratio among the \( IQ \) and the average density of rocks for the watershed represent the chemical weathering rate (\( W_{q} \)- in m/Myr), as expressed in Equation 5.

\[ IQ = F_{\text{w}}(\text{Na}) + F_{\text{w}}(\text{K}) + 2F_{\text{w}}(\text{Ca}) + 2F_{\text{w}}(\text{Mg}) + F_{\text{w}}(\text{SiO}_2) \]  \hspace{1cm} (4)

\[ W_{q} = \frac{IQ}{\rho} \]  \hspace{1cm} (5)

The soil removal rates (\( W_{s} \) in m/Myr) can be calculated through Equation 5; however, the use of corrected TSS annual flux (t/km²/yr) and the average soil density (g/cm³) is necessary instead of \( IQ \) and average density of rocks, respectively (Mortatti et al. 1997, Boeglin and Probst 1998).

**RESULTS**

Table 1 shows the results of \( Q \), pH, EC, T and the concentrations of dissolved ions and SiO₂, TDS, and TSS, with their respective discharge weighted average for the study period.

| Parameter | Unit | Sampling date | C_wet |
|-----------|------|---------------|-------|
| \( Q \) | m³/s | Jun/09 | 28.77 | 32.60 | 81.35 | 67.01 | 110.03 | 228.58 | 230.49 | 118.64 | 98.56 | 71.79 | 48.85 | 31.64 | 95.69 |
| pH | | Jul/09 | 6.8 | 6.9 | 6.9 | 6.9 | 6.7 | 5.6 | 6.6 | 6.6 | 6.8 | 6.9 | 6.9 | 6.9 | 6.7 |
| EC | mS/cm | Aug/09 | 136.9 | 141.8 | 108.6 | 110.9 | 82.2 | 70.9 | 73.7 | 98.1 | 89.5 | 99.0 | 115.0 | 128.0 | 104.6 |
| T | °C | Sep/09 | 16.7 | 17.0 | 16.5 | 19.5 | 26.3 | 26.2 | 27.5 | 25.0 | 26.8 | 25.5 | 22.0 | 20.3 | 22.4 |
| SiO₂ | mg/L | Oct/09 | 34.00 | 28.00 | 13.72 | 13.66 | 14.00 | 9.91 | 9.53 | 11.70 | 11.58 | 12.07 | 16.00 | 28.00 | 13.05 |
| Ca²⁺ | mg/L | Nov/09 | 17.92 | 16.90 | 20.40 | 9.80 | 7.00 | 6.59 | 5.69 | 5.70 | 5.80 | 5.80 | 10.40 | 11.70 | 13.41 |
| Mg²⁺ | mg/L | Dec/09 | 15.15 | 15.92 | 10.59 | 11.41 | 13.87 | 5.64 | 5.60 | 5.61 | 5.60 | 5.60 | 5.60 | 10.40 | 11.70 |
| Na⁺ | mg/L | Jan/10 | 2.26 | 1.90 | 1.70 | 1.83 | 1.66 | 1.65 | 1.67 | 1.70 | 1.75 | 1.90 | 2.10 | 2.10 | 2.30 |
| K⁺ | mg/L | Feb/10 | 51.31 | 45.05 | 36.03 | 38.59 | 35.21 | 25.77 | 30.26 | 38.00 | 36.20 | 37.99 | 39.86 | 43.41 | 34.25 |
| HCO₃⁻ | mg/L | Mar/10 | 18.90 | 15.20 | 7.86 | 8.62 | 4.26 | 3.63 | 4.40 | 5.48 | 6.28 | 7.50 | 8.64 | 10.75 | 6.22 |
| CI | mg/L | Apr/10 | 7.44 | 6.56 | 4.47 | 4.82 | 4.08 | 2.71 | 2.37 | 2.72 | 4.40 | 5.28 | 5.99 | 9.25 | 3.88 |
| SO₄²⁻ | mg/L | May/10 | 4.82 | 3.10 | 2.06 | 2.29 | 1.53 | 0.66 | 0.87 | 1.45 | 3.40 | 4.00 | 5.38 | 5.61 | 2.02 |
| NO₃⁻ | mg/L | June/10 | 0.13 | 0.16 | 0.07 | 0.04 | 0.07 | 0.02 | 0.03 | 0.05 | 0.16 | 0.19 | 0.21 | 0.07 | 0.07 |
| TDS | mg/L | June/10 | 157.55 | 133.81 | 86.61 | 92.63 | 77.05 | 56.29 | 62.45 | 79.69 | 84.64 | 92.16 | 103.28 | 129.74 | 79.64 |
| TSS | mg/L | June/10 | 19.50 | 31.00 | 70.33 | 50.83 | 105.33 | 74.00 | 66.33 | 25.83 | 66.67 | 41.67 | 18.33 | 11.83 | 59.56 |

C_wet: weighted average element/compound concentration for the study period; \( Q \): discharge; EC: electrical conductivity; T: temperature; TDS: total dissolved solids; TSS: total suspended solids.

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the average discharge for the study period (95.69 m³/s) was 1.8 times higher than the historical annual average for the period of 1979–2008 (53.8 m³/s). This is justified by the fact that the rainfall in the study period (2,101 mm) was higher than the historical average (1,276 mm), with a direct impact on the discharge values. During the historical period, a similar occurrence was observed only in 1983, with an annual rainfall of 2,054.0 mm and average discharge of 143.49 m³/s.

The Sorocaba River waters presented a pH close to neutral, ranging from 6.5 to 6.9. The EC showed a significant seasonal variation (annual average of 104.6 mS/cm), with values below 74 mS/cm in the months of highest rainfall and discharge, and values above 135 mS/cm in June and July 2009. During the dry season (May to October), EC values were higher than the expected limit for natural waters, i.e., 100 mS/cm (Hermes and Silva 2004). The T followed the seasonal variation, with the lower values in winter (16.5°C in August 2009) and higher in summer (27.5° C in January 2010).

The concentration of [TSS] was directly related to the discharge (Fig. 3A). According to Probst (1986), for most world rivers the model obtained for the relationship between [TSS] and \( Q (\text{TSS} = aQ^b) \) presents positive \( b \) exponent with values between 1 and 2, indicating that the increase in [TSS] is a function of the discharge increase. This exponent in the model established for the Sorocaba River was 0.7039, indicating that the [TSS] was also influenced by rainfall. This influence is highlighted in the November and December 2009, when the fluvial water sampling was performed after two days of significant precipitation, with accumulated volumes of 45.8 and 25.9 mm, respectively.

On the other hand, the relationship between [TDS] and discharge was inverse and significant (Fig. 3B), which characterizes the dilution process with increasing discharge. Among the dissolved chemical species that compose the TDS, evaluable on a molar basis of \( C_{\text{Na}^+} \), the anionic predominance of HCO\(_3^-\) (33.1%) was verified, followed by Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\), and PO\(_4^{3-}\), while for the cations the greatest participation was Na\(^+\), with 20.6%, followed by Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\), respectively, and the SiO\(_2\) represented 12.8% of the TDS. The relationship “sum of cation vs. sum of anion” (Probst 1992), in meq/L, indicated a deficit of anionic charge in the charge balance (Fig. 3C). It can be attributed to the presence of dissolved organic anions not counted in this study, such as dissolved organic carbon (Probst et al. 1992, Boeglin and Probst 1996, Laraque et al. 2013).

**DISCUSSION**

**Dynamics of fluvial transport in the Sorocaba River basin**

The fluvial fluxes integrate the contributions of the chemical weathering and soil removal processes that occur in natural watersheds. However, nowadays it is also necessary to consider the atmospheric inputs and anthropogenic influences in the fluvial dynamics (Stallard and Edmond 1981, Mortatti et al. 1997, Semhi et al. 2000, Bortoletto Junior et al. 2002, Conceição and Bonotto 2004, Weijden and Pacheco 2006, Mortatti et al. 2008, Conceição et al. 2010, Hissler et al. 2015, 2016).

The \( F_{\text{anthropogenic}} \) of dissolved chemical species, TDS and TSS were quantified in the specific transport form, the result of the product between \( C_{\text{Na}^+} \) and average discharge of the study period weighted by surface of study area, according to the stochastic methodology proposed by Probst (1992). \( F_{\text{rainfall}} \) was represented by the specific input of solute, obtained from the total precipitation in the study period (2,101 mm) and the average concentration of dissolved chemical species obtained by Fernandes (2012).

The \( F_{\text{anthropogenic}} \) for dissolved chemical species, TDS and TSS were obtained using secondary data, despite the uncertainties associated with these data regarding the reality of the studied basin. In relation to dissolved load, it was considering the \( \text{per capita} \) values of the dissolved chemical species present in untreated domestic effluents discharged directly in the river (g/hab/day) established by Mortatti et al. (2008, 2012) for the Médio Tietê basin (SiO\(_2\) = 0.84, Ca\(^{2+}\) = 7.50, Mg\(^{2+}\) = 1.3, Na\(^+\) = 13.1, K\(^+\) = 2.6, HCO\(_3^-\) = 42.0, Cl\(^-\) = 7.1, and SO\(_4^{2-}\) = 12.5), and the total population upstream of the sampling point (1,061,023 inhabitants). The anthropogenic contribution of SiO\(_2\) was considered negligible, such as reported in other studies (Mortatti et al. 2008, 2012). On the other hand, the \( F_{\text{anthropogenic}} \) associated to suspended sediment load was represented by the \( \text{per capita} \) TSS load contained in untreated urban sewage (0.022 kg/hab/day), obtained from average production of untreated urban sewage (100 L/hab/day) and respective TSS average concentration (220 mg/L), both global references data published by Tchobanoglous and Burton (1991), the total population upstream of the sampling point and the respective percentage of urban sewage treatment (17.5%) (IBGE 2010).

**Figure 3.** Relationships (A) between discharge and [TSS] and (B) between discharge and [TDS], (C) and charge balance in the Sorocaba River in the study period, with S+ and S- corresponding to total dissolved cations and anions, respectively.
The fluxes of cations, anions, silica, TDS, and TSS in the Sorocaba River basin are shown in Table 2. The total fluvial flux of TDS was 33% higher than that observed to TSS flux. Among the dissolved chemical species, the HCO₃⁻ presented the highest fluvial flux, corresponding to 43% of TDS, followed by SiO₂⁻ (16.4%), Ca²⁺ (11.8%), Na⁺ (10.1%), and Cl⁻ (7.8%), while the fluvial flux presented by SO₄²⁻, NO₃⁻, K⁺, Mg²⁺ and PO₄³⁻ were lower than 5 t/km²/yr and together represented the remaining 10.9% of TDS. The atmospheric inputs account for 17.3% of the total specific flux of TDS in the Sorocaba River. Regarding the anthropogenic inputs, there was a higher contribution to the dissolved load (ca. 14% of the fluvial TDS) than to the suspended solids load (ca. 4% of the fluvial TSS).

Assuming that the suspended load represents approximately 90% of the total sediment river flux (Walling and Fang 2003), the specific flux of the total suspended solids was determined using the atmospheric inputs. The anthropogenic inputs, after correction of the anthropogenic contributions, the specific flux related to the soil removal (F_w) was approximately 90% of the total sediment river flux (Walling and Probst 2003), both in the Southeastern Brazilian region.

The predominant process of chemical weathering of rocks in the Sorocaba River basin, was determined using the K_e index (Eq. 2) and corresponded to 2.4, which characterizes the total hydrolysis process called allitization, with only aluminum and iron fixed as insoluble hydroxides; when K_e = 2, the process is called partial hydrolysis with monosiallitization, occurring the kaolinite formation; and to K_e = 4 the predominant process is the partial hydrolysis with bisiallitization and is related to the formation of mineral 2:1, such as montmorillonite.

The predominant process of chemical weathering of rocks in the Sorocaba River basin was determined using the K_e index (Eq. 2) and corresponded to 2.4, which characterizes the predominant process of partial hydrolysis with a tendency to monosiallitization, i.e., to the kaolinite stability domain, similar to that observed in the Amazonas River basin (Mortatti and Probst 2003). However, in two watersheds (Tietê and Piracicaba river basins) located in the same region of the Sorocaba River, a different situation was verified, i.e., a tendency to the bisiallitization domain, probably due to extensive agricultural areas with a high degree of soil tillage, fact that may influence the remobilization of major ions instead of silica (Bortoletto Junior 2004).

According to Conceição and Bonotto (2004) and Fernandes et al. (2016a), the main minerals found in the igneous and metamorphic rocks of the Sorocaba River basin are biotite (K(Mg,Fe)₃(Si₃Al)O₁₀(OH)₂), muscovite (KAl(Si₃Al)O₁₀(OH)₂), sillimanite (Al₂SiO₅(OH)), quartz (SiO₂), fluorite (CaF₂), and rutile (TiO₂). The atmospheric/soil CO₂ consumption during the chemical weathering processes in the Sorocaba River basin was obtained using Equation 3 and corresponded to 2.3 × 10⁵ mol/km²/yr. This value was lower than that observed in the Tietê River basin (3.8 × 10⁵ mol/km²/yr, Bortoletto Junior 2004). However, it was higher than other Brazilian watersheds, such as the Amazonas Basin (0.3 × 10⁵ mol/km²/yr, Mortatti and Probst 2003) and Jamari and Jiparana basins (0.8 × 10⁵ and 1.4 × 10⁵ mol/km²/yr, respectively, Mortatti et al. 1992) in northern region, or in the Paraná Basin (0.9 × 10⁵ mol/km²/yr, Gaillardet et al. 1999) and Piracicaba Basin (1.4 × 10⁵ mol/km²/yr, Bortoletto Junior 2004), both in the Southeastern Brazilian region.

Chemical weathering and soil removal rates

The IQ value in the Sorocaba River basin, obtained using Equation 4 and the data of Table 2, corresponded to a flux of 19.1 t/km²/yr, representing 31.4% of TDS flux at the river. The Amazonas and Tietê River basins showed higher fluxes (IQ) than that observed for the Sorocaba River basin.

### Table 2. The annual flux (t/km²/yr) of total suspended solids (TSS), total dissolved solids (TDS), dissolved silica, cations and anions in the Sorocaba River basin.

| Species              | TSS | TDS  | SiO₂   | Ca²⁺  | Mg²⁺  | Na⁺   | K⁺    | HCO₃⁻ | Cl⁻   | SO₄²⁻ | NO₃⁻ | PO₄³⁻ |
|----------------------|-----|------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| F_w                  | 45.59 | 60.97 | 9.99   | 7.22  | 0.71  | 6.15  | 1.34  | 26.22 | 4.76  | 2.97  | 1.54  | 0.06  |
| F_total              | ---  | 10.57 | ---    | 2.99  | 0.12  | 0.40  | 0.28  | 3.60  | 0.71  | 1.24  | 1.18  | 0.05  |
| F_anthropogenic      | 1.78 | 8.54 | 0.08   | 0.74  | 0.13  | 1.29  | 0.26  | 4.13  | 0.70  | 1.23  | ---   | ---   |
| F_a                  | 43.81 | 41.85 | 9.91   | 3.49  | 0.47  | 4.46  | 0.80  | 18.49 | 3.35  | 0.50  | 0.36  | 0.01  |

*Data reported in Fernandes (2012).*
The authors verified a similar soil removal rate, it was almost 3-fold higher than the long-term denudation rates suggested by the literature for the Peripheral Depression, and reinforced that the increase in the denudation rate is mainly related to land use/land cover changes than to the soil type present in the studied area.

CONCLUSION

This study aimed to evaluate the chemical weathering of rocks and soil removal processes that occur in the Sorocaba River basin and allowed a better understanding of the dynamics of fluvial transport of dissolved and suspended solids, of the chemical weathering processes and the atmospheric/soil CO_2 consumption and of the relationship between chemical weathering and soil removal rates. The TSS concentration was directly related to the discharge and influenced by rainfall, with higher concentrations recorded after rainfall events. However, the TDS concentration showed dilution behavior in a wet period. The annual specific flux of TDS was 60.97 t/km^2/yr, but after the atmospheric inputs and anthropogenic contributions (ca. 17 and 14%, respectively) this value was corrected to 41.85 t/km^2/yr and represents the fluvial flux related to the chemical weathering of rocks.

The total annual specific flux of TSS was 45.59 t/km^2/yr, with a small portion derived from the anthropogenic contributions (ca. 4%). The chemical weathering process showed a tendency to monosialitization (R_β = 2.4), with an atmospheric/soil CO_2 consumption rate of 2.3 × 10^5 mol/km^2/yr. The chemical weathering and soil removal rates were 7.2 and 29.8 m/Myr, respectively, indicating a soil thickness reduction. The present soil removal rate in the Sorocaba River basin was almost 3-fold higher than the Cenozoic soil removal rates, reinforcing that the human-landscape systems are complex and affect the natural denudation rates, and, consequently, the present landscape evolution in the State of São Paulo.

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