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INFLUENCE OF DISCHARGE ON SILICATE WEATHERING DYNAMICS OF THE TIETÊ RIVER BASIN: MAJOR CATIONS AND DISSOLVED SILICA APPROACH

J. Mortatti[1,*], J.L. Probst[2], A.M. Fernandes[1,**], B.C. Mortatti[3], H. Oliveira[1,***]
[1]Centro de Energia Nuclear na Agricultura, Universidade de São Paulo
Av. Centenário, 303, CEP 13400-970, Piracicaba, São Paulo, Brazil
[2]Ecole Nationale Supérieure d'Agronomie de Toulouse, Institut National Polytechnique
Avenue de l'Agrobiopole, BP 107, Auzeville Tolosane, 31326 Castanet Tolosan, France
[3]Instituto de Geociências, Universidade Estadual de Campinas,
Rua Cândido Portinari, CEP 13081-970
E-mail: *jmortatt@cena.usp.br; **afernandes@cena.usp.br, ***helder@cena.usp.br

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ABSTRACT

The Tietê river water was investigated in terms of the seasonality of major cations and dissolved silica mainly due to the influences of discharges in the watershed, in order to recognize the main rock weathering type occurring in the basin. With the proposed geochemical model it was possible to identify, after atmospheric and anthropogenic input corrections, the main chemical species released from the silicate weathering in the basin and their relationship with the river discharge. With the Re index calculated for the basin (3.09) it was possible to identify the main weathering process occurring in the basin and the transition of the stability field of monosiallitization to bisiallitization, with no significant seasonal variations in the river water discharge.

RESUMO

O presente trabalho teve por objetivo verificar a sazonalidade dos cátions principais e sílica dissolvida e a influência das vazões na bacia de drenagem do rio Tietê, identificando os principais tipos de alteração dos silicatos predominantes na bacia. O modelo geoquímico proposto, após correção dos aportes atmosféricos totais e antrópicos, permitiu estimar as concentrações das principais espécies químicas dissolvidas nas águas fluviais, oriundas dos processos de alteração de silicatos, em função da vazão. O índice hidrogeoquímico Re calculado para a bacia de drenagem do Tietê (3,09) permitiu identificar as principais vias de intemperismo dos silicatos que ocorrem na bacia de drenagem, evidenciando uma fase de transição do domínio da monosialitização para a bisialitização, com o domínio de minerais 2:1 (ilita), sem significativas variações sazonais.

INTRODUCTION

Hydrogeochemical studies in drainage basins are very important nowadays to understand the behavior of the continental matter transported to the oceans with regard to its seasonal variations and dynamics. According to the literature, about 90% of the dissolved and particulate loads are carried away by rivers to estuarine zones (Gibbs, 1965; Stallard & Edmond, 1983; Meybeck *et al.*, 2003; Probst *et al.*, 1994; Mortatti *et al.*, 2003). River monitoring activities are very important to understand why water chemistry may change from one geological substrate to another showing a spatial evolution of river water chemistry in the basin (Smolders *et al.*, 2004). Other related aspect is the seasonal influence of discharge fluctuations (associated with rainfall input in the drainage basin) on river hydrochemistry (Drever, 1997), where a dilution process can be observed in terms of punctual or diffuse inputs on the basin. According to Probst *et al.* (1992), in drainage basins under natural conditions the main rock weathering processes could be identified only by difference between the river load transported and the respective atmospheric input. On the other side, in basins under strong anthropogenic pressure, the main chemical parameters of the river's pollution should be first evaluated. This is the case with the Tietê river basin located in São Paulo, Brazil, which flows through the first hydrographic zone of the State of São Paulo along an extension of about 592 km and 121 cities including São Paulo (18 million people). The aim of this paper was to identify the seasonal behavior of the major cations and dissolved silica in the weathering dynamics of the Tietê river waters in order to improve hydrogeochemical modeling in a time series of field data that include both data on chemical composition and data on river discharge and rainfall measurements.

CHARACTERIZATION OF THE TIETÊ RIVER BASIN

The Tietê River basin is a unit of the Paraná basin consisting of sub-basins including the Piracicaba, Atibaia, Jaguari, Sorocaba, and Corumbataí river basins, and extends over an area of about 9,060 km^2 with regard to a sampling station located in the city of Tietê. It lies between 21°30' and 24°00' S and 46°00' and 48°00' W, being about 260 km west of the Atlantic Ocean coast (Figure 1).

The Tietê River crosses the metropolitan area of São Paulo which is one of the most industrialized and largest urban centers of South America. The basin under study comprises about 20 million people and receives a large load of industrial and mostly domestic wastes.

The main geological domain is formed by rocks of the crystalline plateau and sedimentary basin, represented basically by granites, gneisses, and basalts mainly in the middle part of the basin along the Depressão Periférica zone. Among the major types of soils that occur in the Tietê River basin, ultisols (55.4 %) and oxisols (28.3 %) cover about 84% of the entire basin area (Oliveira, 1999).

During the studied period (2001-2002) the discharge values for the Tietê River ranged between 54.8 and 352.9 m^3 s^{-1}, averaging 154.6 m^3 s^{-1} at the Tietê sampling station. The total annual rainfall for the Tietê river basin measured by Instituto Agronômico de Campinas (IAC, São Paulo) for the same study period was 1,107 mm.

The Tietê river basin is characterized by a Cwa climate type according to Köppen's classification, with tropical rainy weather characterized by a wet summer. Soil use in the basin comprises an area of intense agricultural (sugarcane and citrus) and industrial occupation (paper, cellulose, textile products, and oil refinery).

METHODOLOGY

Surface waters were collected every fifteen days at the Tietê sampling station using a single stage punctual sampler in the axes of the river current at a depth of 1.5 m, from May 2001 to August 2002, totaling eighteen samples.

After measuring the physicochemical parameters (temperature, pH, electric conductivity) and filtration in the field (Millipore acetate 0.45 µm), the samples were kept at 4°C and sent for analysis of major cations and dissolved silica by ion chromatography using Dionex ICS-90 and Inductively Coupled Plasma-Atomic Emission Spectrometry ICP-AES, respectively.

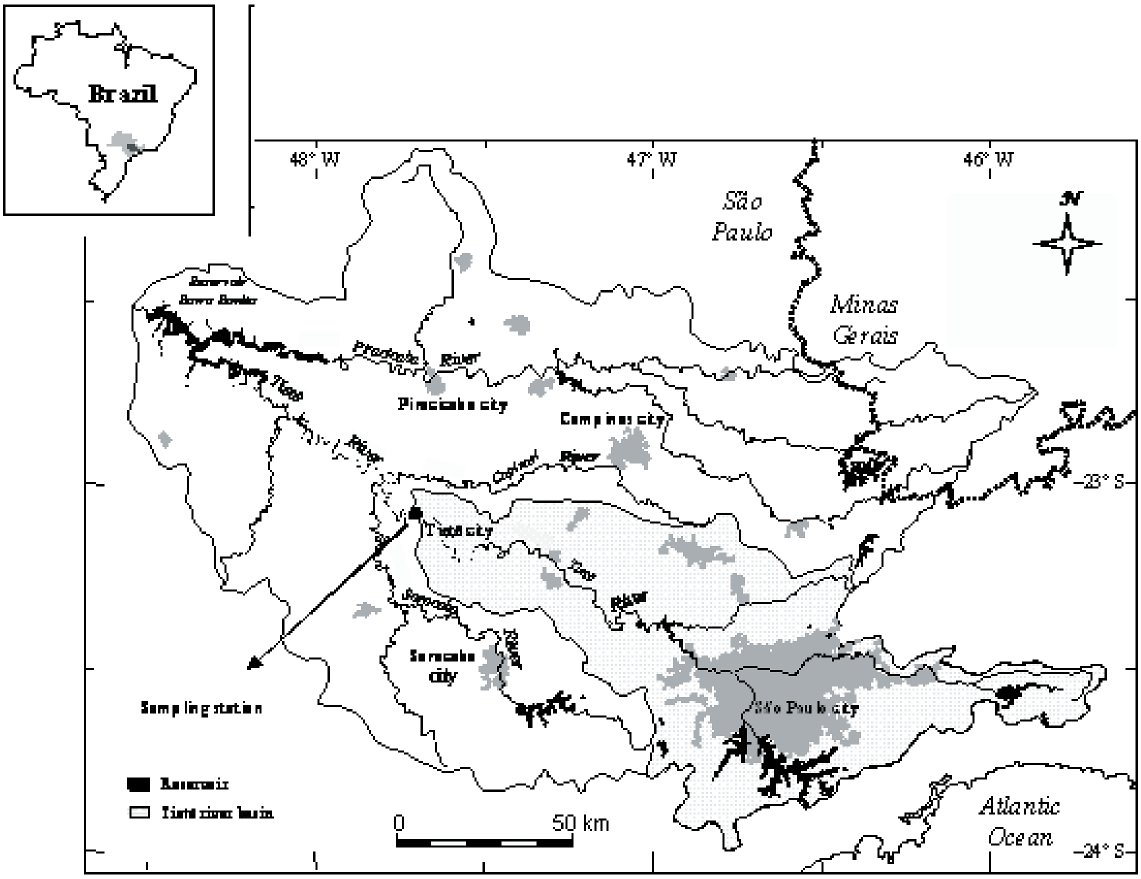

Figure 1: Location map of the Tietê river basin including the sampling station in the city of Tietê.

Twenty-nine rainwater samples were collected in the same period in the city of Tietê (open area of 10 m in diameter) with a bulk-type rain gauge while the dissolved loads from domestic effluents were sampled weekly upstream of the treatment plant during a two-month period. The chemical analyses for rainwater and domestic effluents were performed according to the same analytical protocol already described.

In order to understand the possible seasonal influences on the chemistry of Tietê river water, the frequency of the sampling period was adjusted to cover all parts of the hydrogram, as observed in Figure 2.

The eighteen samples collected during the 2001-2002 period were chemically quantified in terms of major cations and dissolved silica, and the relationship between the main dissolved species and discharge measurements were used to improve modeling in the basin.

The major cation and dissolved silica measurements were made with an accuracy of 0.1 μmol L^{-1}.

Because surface water chemistry depends on weathering processes that occur in the catchment areas, it is very important to understand the retention and release dynamics of the chemical species taking place in the main rock weathering reactions in order to characterize the different stages of this process (Tardy, 1971; Stallard & Edmond, 1983; Meybeck, 1986; Probst *et al.*, 1994).

To determine the degree of rock weathering in a given drainage basin, the molecular ratio Re defined by Tardy (1968, 1969 and 1971) can be used. The Re ratio, expressed by equation 1, was calculated from the molar concentrations

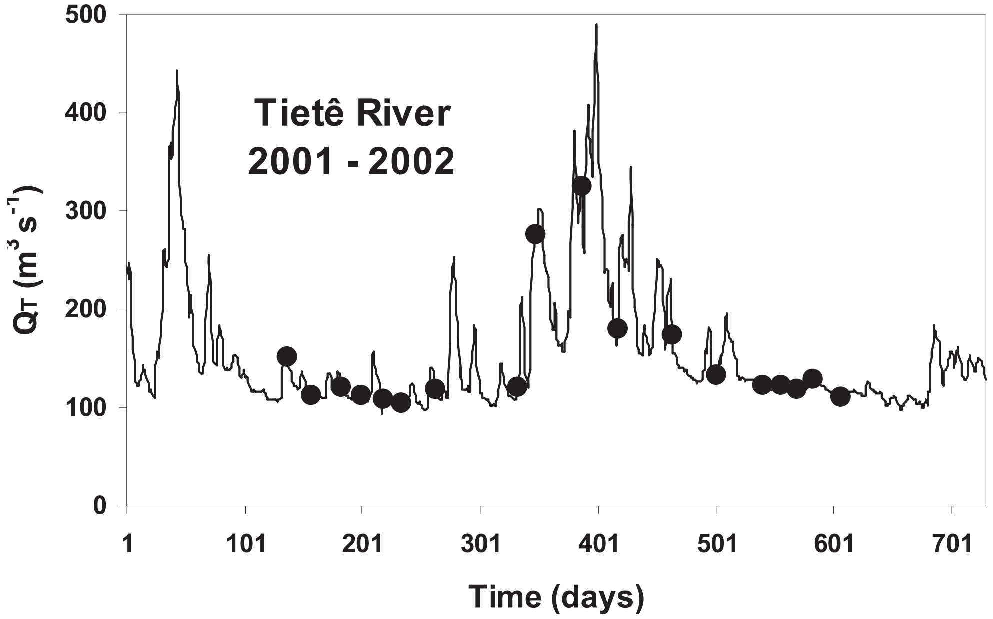

Figure 2: Temporal variation of the Tietê river discharge (QT in m^3 s^{-1}) including sampling points at different stages of the hydrogram.

of the dissolved major cations and silica measured in the surface waters from granite and gneiss substrate.

$$R_e = \frac{3\,K + 3\,Na + 2\,Ca + 1.25\,Mg - SiO_2}{0.5\,K + 0.5\,Na + Ca + 0.75\,Mg} \quad (1)$$

According to Tardy (1968) the Re ratio is equivalent to the (SiO_2) / (Al_2O_3) ratio of secondary mineral neoformation in the soil profile defined by Pedro (1966). The predominant weathering process is characterized in terms of the Re value: if Re = 0, the weathering process is allitization which corresponds to the complete release of basic cations and Si, with Fe and Al remaining (genesis of goethite and gibbsite); if Re = 2, weathering is characterized as monosiallitization, which corresponds to the complete release of basic cations and only some Si is removed with consequent kaolinite formation; if Re = 4, the process is referred to as bisiallitization with neoformation of 2:1 minerals such as smectite, montmorillonite, illite, and others.

In order to understand the main weathering processes that occur in the Tietê drainage basin, it is very important to correct for the influences of the atmospheric and pollution inputs in the river water. The atmospheric input corrections were based on rainwater chemistry in the basin considering the evapotranspiration factor (f) of the concentration for each chemical species in the river water. The f factor was defined as the ratio between total annual precipitation in the basin and mean annual runoff into the Tietê River, in equivalent water height (mm) in the basin.

The pollution signals related mainly to the anthropogenic inputs in the basin are more difficult to correct. The proposed model was involved with the per capita charges of major cations and dissolved silica generated by domestic effluents released into the river without previous treatment. This study was carried out in an urban community (1,500 inhabitants) who collect their domestic effluents in a single waste treatment plant before release into the river.

RESULTS AND DISCUSSION

DISCHARGE AND RIVER CHEMISTRY

The maximum discharge quantified at the Tietê River was 352.9 m^3 s^{-1} during the January 2002 rainy season, while the minimum discharge obtained was during the August 2001 dry period with a value of about 54.8 $m^3 s^{-1}$.

Table 1 reports the chemical results for major cations and dissolved silica for eighteen samples collected from the Tietê River at the station in the city of Tietê during the study period.

According to Probst *et al.* (1992) the dilution of dissolved substances in river water can be understood by considering the relationship between the concentration of dissolved chemical species and water discharge. This relationship between discharge and concentration allows identifying the type of dilution that occurs in the basin. Several models have been proposed to explain the evolution of the concentration of dissolved species as a function of river discharge (Hall, 1971). A power regression model for the Tietê River was tested for major cations and dissolved silica, and is presented in Figures 3, 4, and 5, respectively.

Significant correlations were found between major cations and dissolved silica and Tietê River discharges according to the fitted power regression model ($p \leq 0.001$).

Table 1: Discharges (Q, in $m^3 s^{-1}$) and chemical composition of Tietê river waters for major cations and dissolved silica, including chloride (in μmol L^{-1}), during the 2001-2002 period.

sample	date	Q_T	Ca^{2+}	Mg^{2+}	Na^+	K^+	SiO_2	Cl^-
		($m^3 s^{-1}$)			(μmol L^{-1})			
T1	05/17/01	135.9	472.7	154.8	1652.2	230.2	166.7	1071.9
T2	06/07/01	102.6	575.0	176.9	2260.9	306.9	218.3	1354.0
T3	07/02/01	77.0	612.5	197.4	2391.3	337.6	246.7	1636.1
T4	07/19/01	89.2	542.7	207.1	2326.1	295.5	203.3	1748.9
T5	08/07/01	54.8	750.0	246.8	2969.6	409.2	298.3	1833.6
T6	08/23/01	96.6	585.3	197.4	2130.4	309.5	210.0	1692.5
T7	09/20/01	113.4	500.0	176.9	1826.1	268.5	183.3	1269.4
T8	11/29/01	144.3	437.5	160.4	1434.8	235.3	158.3	1269.4
T9	12/14/01	215.1	410.0	139.9	1217.4	181.6	141.7	987.3
T10	01/22/02	352.9	397.5	123.4	1104.3	161.1	150.0	846.3
T11	02/22/02	177.5	410.0	123.4	1391.3	196.9	165.0	902.7
T12	04/09/02	267.8	390.0	119.3	1217.4	166.2	133.3	818.1
T13	05/17/02	113.4	475.0	148.1	1960.9	268.5	185.0	1356.8
T14	06/25/02	110.3	487.5	144.0	2021.7	278.8	196.7	1399.2
T15	07/11/02	85.6	587.5	181.0	2100.0	296.7	200.0	1551.5
T16	07/24/02	104.9	510.0	156.3	2143.5	281.3	191.7	1483.8
T17	08/07/02	101.8	502.5	156.3	1934.8	271.1	198.3	1215.8
T18	08/30/02	87.0	545.0	176.9	2365.2	329.9	233.3	1887.2

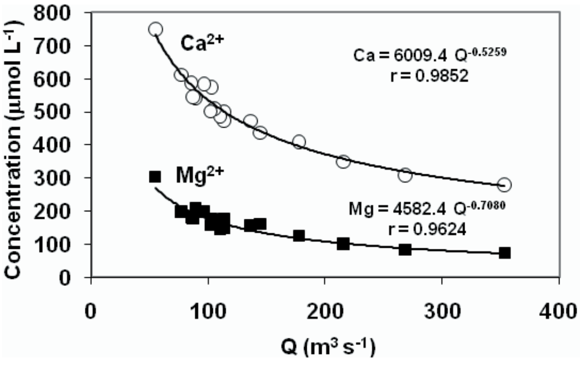

Figure 3: Ca^{2+} and Mg^{2+} distributions as a function of Tietê river discharge during the 2001-2002 period.

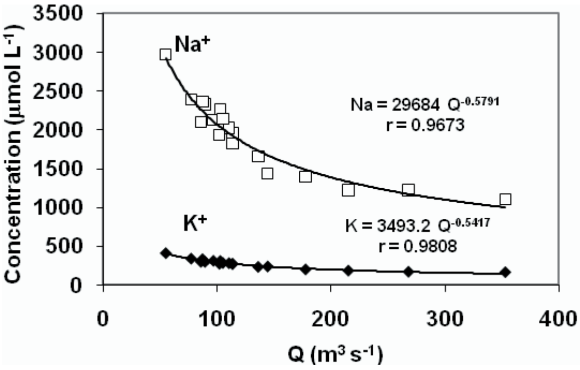

Figure 4: Na^+ and K^+ distributions as a function of Tietê river discharge during the 2001-2002 period.

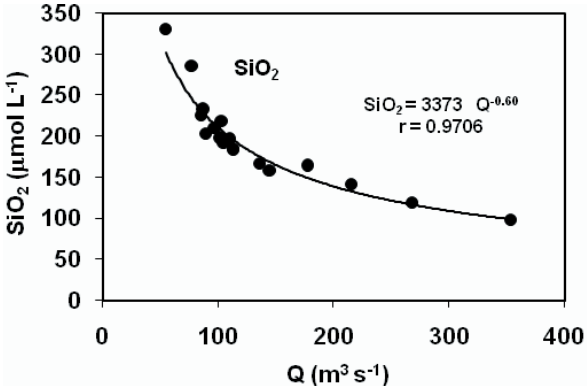

Figure 5: Dissolved silica distributions as a function of Tietê river discharge during the 2001-2002 period.

The observed dilution process of major cations and dissolved silica in the Tietê river basin can be considered in terms of high water discharge influence (including punctual inflows) and diffuse inputs on the drainage basin, which are related to rock weathering dynamics.

The observed behavior of major cations as a function of discharge is common in large rivers where an effective recharge process occurs in the basin (Stallard & Edmond, 1983; Meybeck, 1986; Probst, 1992; Mortatti *et al.*, 1997; Boeglin & Probst, 1998).

The mean concentration of SiO_2 in the Tietê River during the 2001-2002 period, 193.3 µmol L^{-1}, was higher than the mean reported by Meybeck (1979) for some major rivers in the world (173 µmol L^{-1}). The relationship between SiO_2 concentrations and discharge shows a good correlation with a tendency of dilution in river water. This tendency was not verified by Semhi *et al.* (2000) for the Garonne river basin in France, where the concentration of dissolved silica increased during high water periods, being influenced by the removal of solutes from the soil during the high water period.

The sources of dissolved silica in Tietê river water are mainly related to silicate-weathering processes that occur in the basin rather than derived from surface soils.

The power regression model adjusted to the major cations and dissolved silica for the Tietê River allowed estimating the concentrations of the related chemical species n river water by knowing only the daily nean discharge at the Tietê sampling station at any time.

ATMOSPHERIC INPUT

The contribution of the atmospheric nput to the amounts of major cations and dissolved silica in the Tietê river water was obtained by sampling incidental rainwater in the drainage basin (mm d^{-1}) and by the corresponding chemical analysis of those dissolved species. Table 2 shows the chemical composition of incidental rainwater collected in the Tietê river basin during the study period.

The concentration evapotranspiration factor (f) was calculated as the ratio between total annual precipitation (P) and mean annual runoff into the Tietê river (Q), in equivalent water height (mm) in the drainage basin during the period studied, according to equation 2:

$$f = \frac{P}{Q} \qquad (2)$$

Considering 1,107 mm the average of the total annual precipitation during the 2001-2002 period and 538.1 mm the mean annual discharge for the Tietê river (in equivalent water height in the basin), the calculated value for the (f) factor was 2.06. This value was used to correct, as a concentration factor, the amounts of major cations and dissolved silica in rainfall at the basin.

ANTHROPOGENIC INPUTS

The contribution of anthropogenic inputs to the amounts of major cations and dissolved silica in the Tietê river water was estimated in terms of charges per capita of major cations and dissolved silica generated by the domestic effluents released into the river without previous treatment, initially considering an urban community (1,500 inhabitants) who collects their domestic

Table 2: Chemical composition of rainwater in the Tietê river basin in terms of major cations and dissolved silica, including chloride (in µmol L^{-1}) collected during the 2001-2002 period.

date	P	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SiO_2	Cl^{-}
	(mm d^{-1})			(µmol L^{-1})			
08/28/01	24.4	31.8	11.9	20.9	10.5	5.7	42.3
09/13/01	20.0	35.0	23.4	42.0	26.3	9.3	71.7
10/01/01	57.9	17.5	6.2	12.6	2.6	2.5	15.0
10/18/01	14.7	33.0	20.6	36.3	15.3	11.1	64.9
11/11/01	38.9	26.0	10.0	21.7	4.9	3.9	45.7
11/13/01	42.0	18.3	7.4	19.6	2.6	2.5	16.9
11/28/01	29.6	27.0	10.3	12.6	9.2	4.3	36.7
12/16/01	40.7	10.5	2.5	7.5	1.0	2.1	16.9
12/28/01	23.7	32.2	8.6	16.1	6.4	7.5	61.5
12/29/01	22.4	28.0	10.0	20.0	6.2	5.0	50.8
01/08/02	44.0	20.0	4.1	7.0	1.3	2.9	16.9
01/12/02	53.2	12.0	2.5	6.5	1.3	2.9	6.5
01/13/02	28.1	24.8	7.2	15.6	4.8	3.9	42.3
01/26/02	27.7	19.5	5.8	23.0	3.8	2.9	20.9
01/28/02	52.9	12.0	3.7	15.4	1.0	1.8	11.3
01/29/02	36.7	27.3	8.2	17.4	4.1	2.9	27.4
02/01/02	85.0	15.7	4.9	9.6	0.5	1.8	15.0
02/06/02	35.5	19.0	4.1	8.7	2.6	1.4	8.5
02/21/02	39.0	22.3	7.8	9.1	1.5	2.1	13.3
03/03/02	30.4	27.5	7.4	17.4	5.1	4.6	20.9
03/14/02	24.3	32.5	15.1	27.4	7.7	8.6	50.8
03/20/02	58.3	12.5	4.1	8.7	2.6	1.1	14.1
03/24/02	95.4	11.3	2.5	7.8	1.3	0.7	14.1
05/03/02	11.5	32.0	14.0	35.1	9.2	5.7	36.7
05/05/02	16.8	31.0	7.4	19.3	6.0	3.5	25.4
05/19/02	27.4	30.0	11.9	11.7	4.6	5.8	33.9
05/21/02	51.7	13.0	2.1	5.3	1.0	1.7	11.3
08/01/02	34.6	25.0	8.6	14.8	7.7	7.3	50.8
08/02/02	21.8	25.0	4.1	14.2	12.8	3.8	43.4

effluents in a single waste treatment plant before release into the river.

The main objective of this proposed model was to quantify the potential pollution signal from domestic effluents released directly into the river and then expand the result to the entire drainage basin.

Table 3 shows the mean domestic effluent concentrations for major cations and dissolved silica, the total load of the effluent

Table 3: Concentrations of domestic effluents ($C_{Effluent}$), effluent input rates at the Tietê river (in tons per day and grams per person per day) and effluent input rates at Acheres waste treatment

Chemical species	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SiO_2	Cl^{-}
$C_{Effluent}$ (Tietê/São Paulo) (µmol L^{-1})	930.0	267.4	2830.4	327.4	70.0	993.0
Effluent input (Tietê river) (tons per day)	112.5	19.5	196.5	39.0	12.7	106.5
Effluent input (Tietê river) (grams per person per day)	7.5	1.3	13.1	2.6	0.8	7.1
Effluent input (Acheres/Paris/French) (grams per person per day)	3.3	1.9	17.5	4.1	0.5	17.3

input in the basin, and the specific load input in the city of Tietê (São Paulo/Brazil) as compared with the specific load input obtained by Thibert (1994) for the Acheres waste treatment station (Paris/France). The specific loads obtained at the city of Tietê were very close to the specific loads observed at the Achères station in France. It can be observed that Ca^{2+} was much more concentrated in our domestic effluents (7.5 grams per person per day) than the French effluents (3.3 grams per person per day). For dissolved silica this tendency was similar, with 0.8 and 0.5 grams per person per day for Tietê and Acheres, respectively.

It is important to observe that in both models the anthropogenic input was considered constant throughout the year, and the specific per capita inflow was extended to the entire basin.

The total load of domestic effluents released into the Tietê river was calculated in terms of the modeled daily discharge in order to quantify the net concentrations of major cations and dissolved silica in the effluents during the study period.

The distributions of major cations and dissolved silica in the Tietê river water after correcting for atmospheric and anthropogenic inputs over the basin relative to discharge measurements during the 2001-2002 period can be observed in Figures 6 to 10.

ROCK WEATHERING PROCESS

To determine the degree of rock weathering for the Tietê river basin, the molecular ratio Re, which involves the major cations and dissolved silica, defined by Tardy (1968, 1969, and 1971) was used.

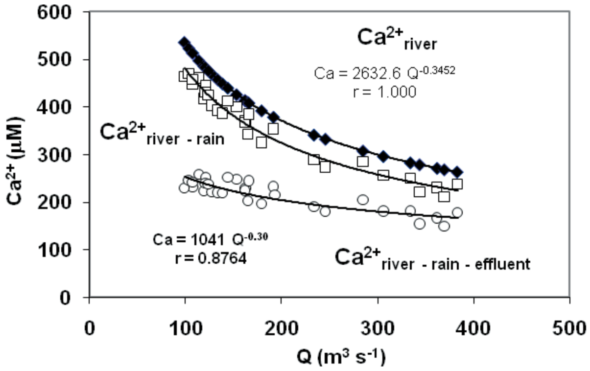

Figure 6: Ca^{2+} distribution models in Tietê river water as a function of discharge measurements after correction of atmospheric and anthropogenic inputs in the basin.

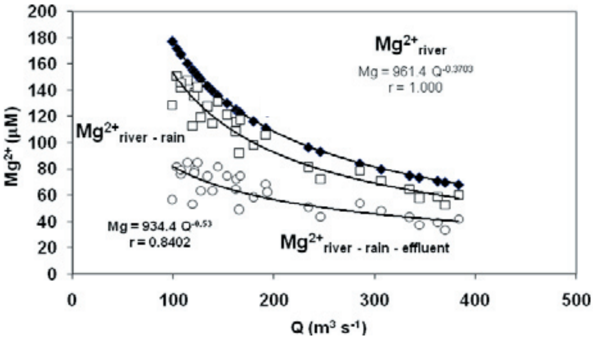

Figure 7: Mg^{2+} distribution models in Tietê river water as a function of discharge measurements after correction of atmospheric and anthropogenic inputs in the basin.

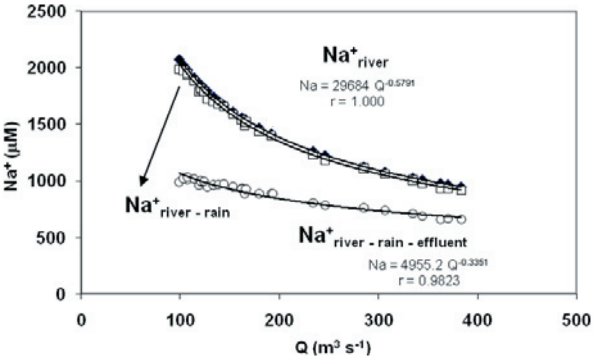

Figure 8: Na^{+} distribution models in Tietê river water as a function of discharge measurements after correction of atmospheric and anthropogenic inputs in the basin.

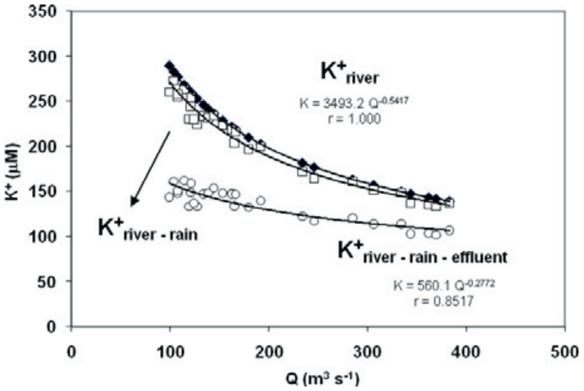

Figure 9: K^{+} distribution models in Tietê river water as a function of discharge measurements after correction of atmospheric and anthropogenic inputs in the basin.

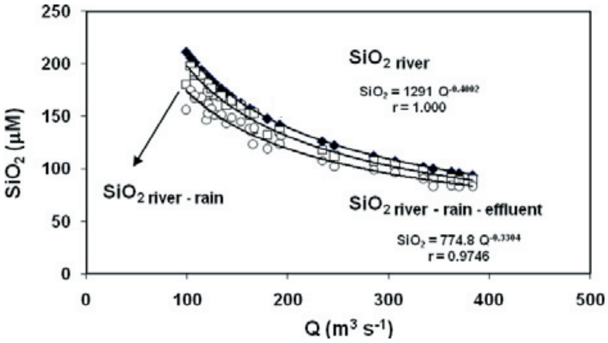

Figure 10: SiO^2 distribution models in Tietê river water as a function of discharge measurements after correction of atmospheric and anthropogenic inputs in the basin.

Before calculations, the corrections related to atmospheric and anthropogenic inputs in river water chemistry should be performed; however, other important corrections should be taken into account due to the fact that the Re value is only valid for surface waters from granite and gneiss substrates. Consequently, the atmospheric and anthropogenic input corrections alone are not sufficient to quantify the main rock weathering process in the Tietê river basin.

In order to know the major cations related to silicate weathering, the geochemical model MEGA developed by Amiotte-Suchet & Probst (1996), adapted by Mortatti & Probst (2003) for silicate rock weathering in the Amazon basin and for chemical erosion in the Piracicaba river basin (Mortatti *et al.*, 2003) was used. This model is based on the stoichiometric dissolution or hydrolysis of the various minerals that are likely to react.

After atmospheric and anthropogenic corrections, the main assumptions of the proposed model were:

- all Cl is associated with Na (saline films in the soils and/or evaporitic rocks);

- all Na after subtraction of the NaCl component is derived from silicate rock weathering;

- all K may be considered as derived from silicate weathering;

- Ca and Mg are derived from carbonate dissolutions and silicate weathering.

The main difficulty in such an approach is to distinguish between Ca and Mg silicate weathering contributions and carbonate dissolution to the riverine fluxes. This contribution was calculated by using the (Na + K) / (Ca + Mg) ion ratio in stream water draining only silicate rocks, whose value is about 1.5 (Probst *et al.*, 1994; Amiotte-Suchet, 1995; Amiotte-Suchet & Probst, 1996). The following equations were used to evaluate Ca and Mg from silicate weathering and carbonate dissolution :

$$(Na+K)_{sil} / (Ca+Mg)_{sil} = 1.5 \qquad (3)$$

$$(Ca+Mg)_{carb} = (Ca+Mg)_{river} - (Ca+Mg)_{sil} \qquad (4)$$

$$Ca_{carb} = (Ca+Mg)_{carb} - Mg_{carb} \qquad (5)$$

$$Mg_{carb} = 0.2\,(Ca+Mg)_{carb} \qquad (6)$$

The above propositions were used for Tietê river waters to characterize the main weathering process occurring in the basin during the 2001-2002 period. The values obtained for Re from the corrected concentrations of major cations and dissolved silica, including chloride, can be observed in Figure 11.

The average Re value calculated for the Tietê river basin was 3.09 with a minimum value of 2.81, corresponding to the dry period, and a maximum value of 3.31 for the rainy season. It means that no significant seasonal variation could be observed in the Tietê river basin and the calculated value was settled between the influence field of kaolinite, monosiallitization (1:1 clay minerals), and bisiallitization (2:1 clay minerals). These results agree with the clay minerals observed by Nascimento (2003) in bottom sediments for the Tietê river basin, showing significant occurrences of kaolinite and illite in the region of study.

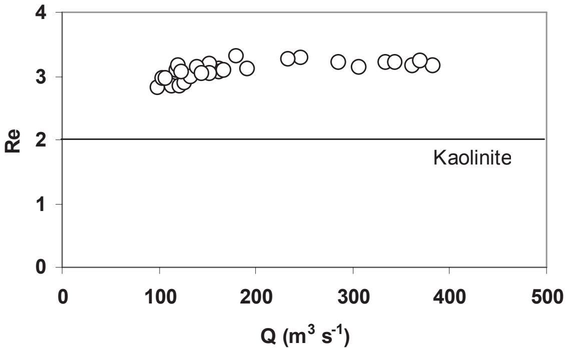

Figure 11: Relationship between Re values in Tietê river waters and discharge Q (in m^3 s^{-1}) measured during the 2001-2002 period.

CONCLUSION

The Tietê river water proved to be highly influenced by discharge according to the observed seasonal variations, including the dilution model for each chemical species and also by the weathering processes that occur in the basin. The power regression model adjusted to major cations and dissolved silica allowed to estimate the concentrations of the related chemical species in river water by knowing only the daily mean discharge at the Tietê sampling station at any time. The contributions of the atmospheric input to the amounts of major cations and dissolved silica in Tietê river water were obtained by acquiring knowledge about the basin's rainwater chemistry, considering the evapotranspiration factor (f) that controls the concentrations of chemical species in the river coming from rainwater in the drainage basin. The contributions of anthropogenic inputs in Tietê river water were determined by quantifying the potential pollution signal from domestic effluents released directly into the river without any treatment. Na and Ca were considered the most significant chemical species in the effluent inputs in Tietê river water with individual loads of 13.1 and 7.5 grams per person per day, respectively. Using the geochemical model proposed to identify the main chemical species released from silicate weathering it was possible to calculate the Re index for the Tietê river basin; the mean value of 3.09 obtained showed a mixed influence of the main weathering types that occur in the catchment, associating the stability field of kaolinite (monosiallitization, 1:1 clay minerals) and illite (bisiallitization, 2:1 clay minerals) with no significant seasonal variations.

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(Footnotes)

[1] To whom the correspondence should be sent:jmortatt@cena.usp.br