

Use of U-isotope disequilibrium to evaluate the weathering rate and fertilizer-derived uranium in São Paulo state, Brazil

F. T. Conceição · D. M. Bonotto

Abstract The U-disequilibrium method was utilized to evaluate the velocity of alteration of rocks and fertilizer-derived uranium in the Corumbataí River basin, São Paulo state, Brazil. The Corumbataí River basin is affected by the continuous use of fertilizer-derived uranium utilized in sugar cane crops, increasing the dissolved uranium concentration in the Corumbataí River (Santa Terezinha station) in the wet period to 43%. The weathering rate in the Corumbataí River basin utilizing the U-isotope modeling was 0.0265 mm/year (corresponding to 38,000 years to weather 1 m of rock under actual climatic conditions). However, when the inputs of anthropogenic uranium were considered, then a weathering rate of 0.022 mm/year (corresponding to 45,500 years to weather 1 m of rock) was determined. The removed material in the Corumbataí River basin is mainly from two sub-basins (the Cabeças River and Passa Cinco River), where the sandstones weather easier than the siltstones and claystones in the basin.

Keywords Weathering rate · Uranium · Phosphate and anthropogenic influences · Brazil

Introduction

The determination of the weathering rate of rocks is of interest to geoscientists, as this phenomenon provides the parameters needed for a better soil exploration, assisting with the establishment of agricultural fields and human settlements. Many studies have used major element concentrations (sodium, calcium, potassium and magnesium) to evaluate the chemical weathering rate (Johnson and others 1968; Gibbs 1970; Moreira-Nordemann 1977; Paces 1986; Koptsik and others 1999; Land and others 1999), despite the difficulties of correcting their intake from rainwater. This research evaluated the chemical weathering rate of rocks using ^{238}U as a natural trace element and the assumption that it is not contained in the rain, following the approach by Moreira-Nordemann (1977). The natural uranium comprises the isotopes ^{238}U , ^{234}U and ^{235}U , which have the same geochemical behaviour and whose relative proportions, under radioactive equilibrium conditions, are 99.28, 0.0054 and 0.72%, respectively (Coward and Osmond 1974). U-234 is radiogenic, being generated in the U-238 decay series after one alpha decay and two beta decays, i.e. ^{234}Th (24.1 days) and ^{234}Pa (1.18 min). In the alteration front, ^{234}U is preferentially mobilized to ^{238}U when rock weathers (Ivanovich and Harmon 1992). Measurements of the $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) in rocks, soils and waters have allowed the calculation of the solution coefficient for the uranium characteristic of the region, which allows the evaluation of the time necessary to weather 1 m of rock under actual climatic conditions (Moreira-Nordemann 1980, 1984). This study reports on the use of U-isotope modeling to evaluate the weathering rate, where the ^{238}U concentration and AR were determined for surface waters, rocks and soils of the Corumbataí River basin, an important sedimentary basin in São Paulo state, Brazil. This basin was chosen because of its unique aspect of comprising all stratigraphic units from the giant Paraná sedimentary basin (Paleozoic–Cenozoic), which covered 70% of the whole São Paulo state. This state produces much of the Brazilian sugar cane, and, consequently, a large quantity of fertilizers is used in agricultural activities. Applications of chemical fertilizers increase the phosphate and uranium concentrations in soils, resulting in impacts on natural systems, such as increasing nutrient and uranium

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concentration in surface waters, soils and sediments. An additional aspect is that the Corumbataí River basin is populated and affected by domestic and industrial wastes, as well as by agricultural processes and wastes derived from sugar cane crops. Herewith, this work also describes the results obtained in evaluating the fertilizer-derived uranium in surface waters of the Corumbataí River basin, with the purpose of identifying how possible anthropogenic inputs are affecting the dissolved ^{238}U and AR data, as the U-isotope modeling depends on these parameters.

Theoretical background

The U-isotopes method to determine the weathering rate of rocks was first applied in Preto and Salgado River basins (Moreira-Nordemann 1980, 1984). The quantity of removed weathered matter, W ($\text{ton km}^{-2} \text{ year}^{-1}$), per unit of surface and per unit of time is determined as follows:

$$W = E_E D / E_R S \quad (1)$$

where E_E is the weighted average U concentration in river water; E_R is mean concentration of U in rocks; D is mean discharge of the river; and S is surface of the basin.

The weathering rate of rocks in the basin (v) depends on the density (ρ) of rocks and of the coefficient of dissolution (k) of the elements partly soluble during weathering, according to the following formula:

$$v = W / k\rho = E_E D / k\rho E_R S \quad (2)$$

where v is in cm/year , E_E $\mu\text{g/L}$, E_R $\mu\text{g/g}$, D L/year , ρ g/m^3 and S cm^2 .

For uranium, the solubility coefficient may be expressed by:

$$k = (A_R - A_S) / (A_E - A_S) \quad (3)$$

where A_R , A_E and A_S are the mean $^{234}\text{U}/^{238}\text{U}$ ratios in rocks, waters and soils, respectively.

Physiographic features

The Corumbataí River basin extends over an area of about $1,581 \text{ km}^2$ in the middle-east part of the São Paulo state (Fig. 1). It occurs as an eroded belt in the cuestas zone of the Depressão Periférica geomorphological province (Penteado 1976). Such a province delimits the northeastern edge of the basaltic flows in the Paraná sedimentary basin and the crystalline plateau, having been submitted to smoothing processes during past geological time.

The Corumbataí River basin is a sub-basin of the giant Paraná sedimentary basin which extends over an area of $1,700,000 \text{ km}^2$ ($1,000,000 \text{ km}^2$ in Brazilian surface) (França and Potter 1988). Several stratigraphic units of the Paraná basin (Paleozoic–Cenozoic) crop-out in it [IPT (Technological Research Institute of São Paulo State) 1981]: the Tubarão Group comprising the Itararé Sub-group

(sandstones, conglomerates, diamictites, tillites, siltstones, shales and rythmites) and the Tatuí Formation (siltstones, shales, silex and sandstones with local concretions); the Passa Dois Group comprising the Irati Formation (siltstones, mudstones, black betuminous shales and limestones) and the Corumbataí Formation (mudstones, shales and siltstones); the São Bento Group comprising the Pirambóia Formation (sandstones, shales and muddy sandstones), Botucatu Formation (sandstones and muddy sandstones), Serra Geral Formation (basalts and diabases) and related basic intrusives; and different types of Cenozoic covers such as recent deposits, terrace sediments and the Rio Claro Formation (sandstones, conglomerate sandstones and muddy sandstones). Among the major types of soils occurring in the Corumbataí River basin, yellow-red podzols and latossols cover about 65% of the area of the basin (Köffler 1993).

The Corumbataí River flows from the cuestas zone to the confluence with the Piracicaba River. Rio Claro city is the most important municipality in the basin, with 170,000 inhabitants. Monthly measurements of the flow rate over the last 26 years were performed at Santa Terezinha, close to the confluence with the Piracicaba River (Fig. 1). The flow rate frequency distribution (Fig. 2) indicates that 37.4% of the observed values are between 10 and $20 \text{ m}^3 \text{ s}^{-1}$. The average monthly flow is $26.4 \text{ m}^3 \text{ s}^{-1}$, maximum value $168.4 \text{ m}^3 \text{ s}^{-1}$ (February 1995) and minimum value $6.0 \text{ m}^3 \text{ s}^{-1}$ (September 1994) (Conceição 2000). The tropical climate of the region is characterized by a wet summer (October to March) and dry winter (April to September) (Inácio and Santos 1988). The area often has 55–65 days of rain per year, with more than 80% of the precipitation falling between October to March (Bonotto and Mancini 1992). The mean annual rainfall corresponds to 1,572 mm (Conceição 2000). Figure 3 shows the average monthly rainfall during the last 21 years and the average monthly flow rate in the last 26 years at the Corumbataí River; as expected, flow in the river is directly bounded to rainfall.

Sampling methods

Six water samples from the Corumbataí River at Santa Terezinha station (Fig. 1) were collected for hydrochemical and U-isotope analyses (Table 1) on a monthly basis between 08/13/1998 and 01/20/1999. Water samples from the Cabeças River and Claro stream were collected for U-isotope analyses in 08/13/1998. Rock and soil samples were collected throughout the whole basin, taking into account the geological context, the kinds of rocks and their abundance or spatial representativity (Fig. 1; Tables 2 and 3).

Each water sample was divided into three aliquots and stored in polyethylene bottles under different conditions. Raw water was used for pH, dissolved oxygen, conductivity and dry residue measurements. Dissolved oxygen was measured in the field, whereas pH and conductivity were measured not more than 6 h after sampling. Filtered

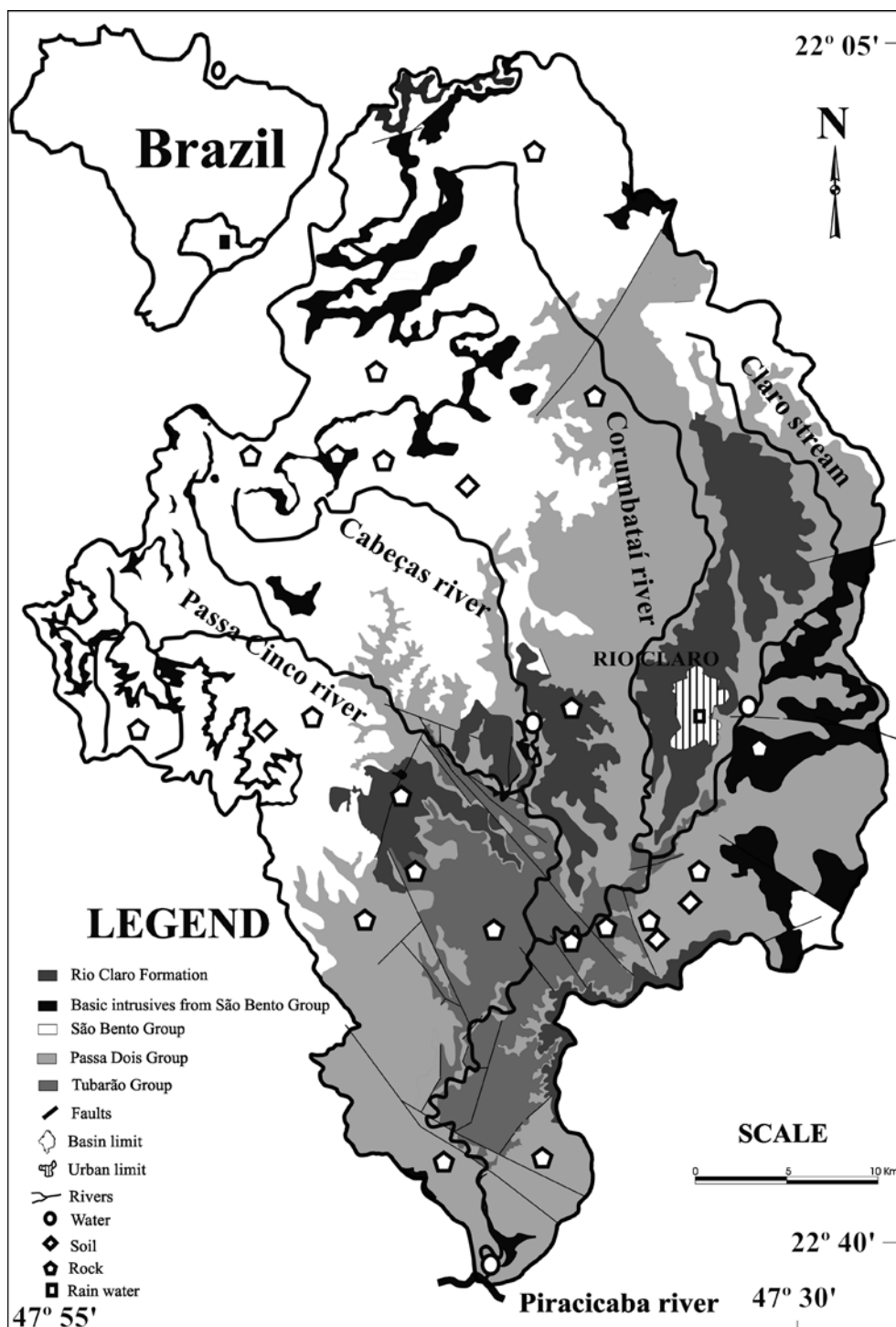


Fig. 1

The Corumbataí River basin and location of sampling points. [Modified from Centro de Análise e Planejamento Ambiental (2001)]

water (0.45- μ m Millipore membrane) was used for alkalinity and chloride determinations. Filtered and acidified water (HNO_3 , pH <2) was used for major ions and uranium determinations.

The dissolved major cations Na and K were analysed by atomic absorption spectrometry (AAS) and Ca and Mg by inductively coupled plasma atomic emission spectrometry (ICP-AES). Sulfate (barium sulfate colorimetric method; range: 0 to 70 \pm 0.9 mg/L), phosphate (cadmium reduction method; range: 0 to 3 \pm 0.01 mg/L)

and nitrate (cadmium reduction method; range: 0 to 20 \pm 0.4 mg/L) were measured by a Hach DR 2000 spectrophotometer (Hach 1992). Alkalinity was measured by titration with 0.02 N sulfuric acid (Hach 1992) in the range of 1 to 500 \pm 0.2 mg/L. Chloride was evaluated by potentiometry (0.1 to 100 \pm 0.02 mg/L), according to the procedure described by Tonetto (1996). Dissolved oxygen was measured in the field, whereas pH and conductivity were measured not more than 6 h after sampling.

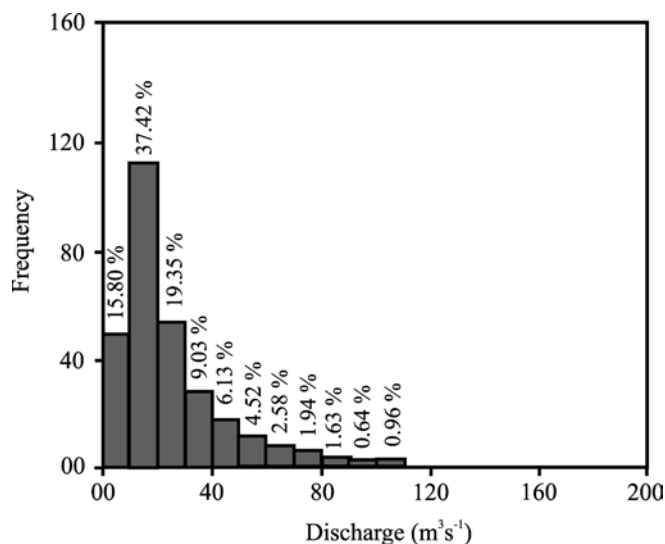


Fig. 2
Frequency of discharge (m^3/s) at the Corumbataí River over the last 26 years

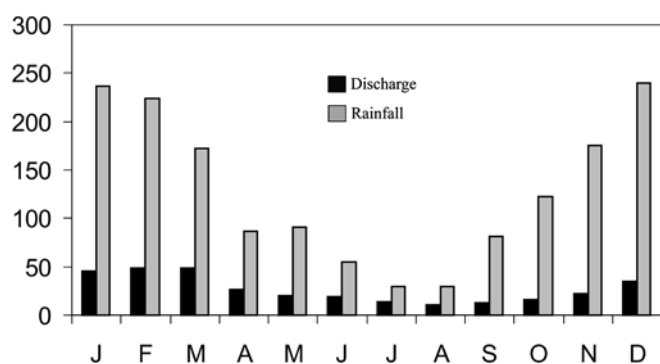


Fig. 3
Monthly rainfall (mm/year) in the last 21 years and discharge (m^3/s) over the last 26 years in the studied area

Uranium concentration and isotopic composition of all samples were determined using standard alpha spectrometric techniques (Osmond and Cowart 1976; Bonotto 1986; Ivanovich and Harmon 1992), where ^{232}U was the spike utilized. About 1.5 g of each rock and soil sample was crushed to 200 mesh (0.074 mm), placed in an acid digestion bomb similar to Parr 4575 at 150 °C and under internal pressures of 1,200 psig (84.37 kg cm^{-2}), and brought into complete solution with HF, HNO_3 and HCl (Bonotto 1996). The solution was heated to dryness, the residue was dissolved in 8 M HCl, and then the procedure was the same as utilized for waters. Uranium was co-precipitated with $\text{Fe}(\text{OH})_3$, iron was extracted with isopropyl ether and U was separated from Th and other elements by the anion exchange resin. The aliquot containing U was transferred to an electrode position cell, and U was deposited on a stainless-steel planchet after 3 h at a current density of 1 A cm^{-2} (Bonotto 1996). The counting of alpha activities was with an Si(Au) surface barrier detector. The concentration of dissolved uranium was calculated by isotope dilution from the counting rates

of ^{238}U and ^{232}U peaks, and AR was calculated from the counting rates of ^{238}U and ^{234}U peaks.

Results

Hydrochemistry

Table 1 shows the physical and chemical parameters for the six sampled waters of Corumbataí River (Santa Terezinha station). The pH values obtained during the 6 months of sampling are close to neutral. No significant relationship was found between the conductivity and dry residue because raw water was analyzed and the dry residue reflected the presence of suspended matter. When the chemical data are plotted on a standard Piper (1944) diagram (Fig. 4), it is possible to verify a variable water chemistry during the sampling period, primarily caused by variable Ca^{2+} and HCO_3^- - SO_4^{2-} contents.

According to CONAMA [CONAMA (National Council for Environment) 1986], the results obtained for dissolved oxygen and major anions suggest that the analysed waters belong to class 2 (fresh waters with salinity equal or lower than 0.50‰, which are appropriate to domestic users after conventional treatment). However, in terms of phosphate, all samples exhibited values higher than the maximum permissible concentration limit for fresh waters belonging to class 2 (0.025 mg/L). Data for dissolved nitrate (NO_3^-) generally clustered near the maximum permissible concentration limit of 10 mg/L, despite the limited availability of natural phosphorus and nitrogen from sedimentary rocks in the basin. Excess nutrients from fertilizer have been suggested to be the major factor responsible for increased eutrophication of reservoirs or stagnant waters elsewhere (Tundisi 1986).

Uranium in water

Table 1 reports the uranium concentration and AR data for all samples collected at Corumbataí River (Santa Terezinha station). The mean weighted uranium concentration was calculated by the following formula:

$$U_E = \frac{\sum_{i=1}^n (U_i V_i)}{\sum_{i=1}^n i(V_i)} \quad (4)$$

where U_i is uranium concentration for the i th measurement and V_i is flow of the river on the day for the i th measurement.

The mean uranium concentration of the river water is 0.25 $\mu\text{g/L}$, which increased progressively until January 1999. The average weighted $^{234}\text{U}/^{238}\text{U}$ activity ratio for the same waters corresponded to 1.82, suggesting the occurrence of preferential leaching of ^{234}U relative to ^{238}U , a process extensively discussed by Dooley and others (1966).

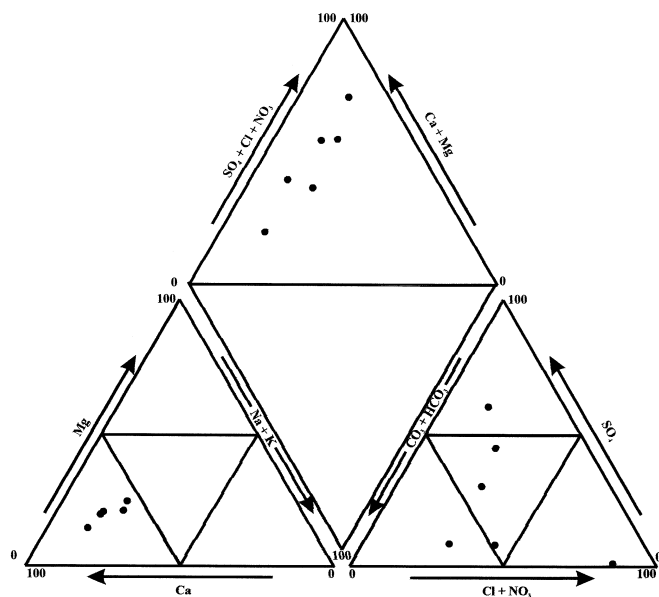
Uranium in rocks

Table 2 contains the uranium concentration and AR in rocks of the Corumbataí River basin, which were sampled taking into account the spatial representativity of the various formations present in the area. The uranium

Table 1

Physical, chemical and isotopic parameters for waters of the Corumbataí River (Santa Terezinha station)

Parameter	Unit of measurement	Date of sampling						Weighted mean
		08/13/1998	09/23/1998	10/21/1998	11/18/1998	12/23/1998	01/20/1999	
pH		6.7	6.8	7.3	6.5	6.8	6.9	6.8
Conductivity	µS/cm	284.4	170.7	208.0	206.0	179.8	182.8	196.34
Dissolved oxygen	mg/L	6.7	6.9	7.3	6.5	7.3	6.8	6.9
Dry residue	mg/L	191	127	154	195	217	172	178
Na	mg/L	6.00	7.56	8.34	10.71	6.93	6.19	7.23
Ca	mg/L	25.00	18.58	17.68	16.39	16.79	12.09	16.38
K	mg/L	8.72	4.16	3.55	4.65	2.89	2.16	3.69
Mg	mg/L	6.00	5.51	6.71	4.72	6.61	6.77	6.28
SO ₄ ²⁻	mg/L	17	48	44	21	32	37	34.34
NO ₃ ⁻	mg/L	9.24	10.56	8.36	13.64	13.20	9.24	10.58
Cl ⁻	mg/L	1.08	4.45	4.11	6.16	4.46	3.80	4.01
HCO ₃ ⁻	mg/L	40	30	30	30	25	26	28.68
PO ₄ ³⁻	mg/L	0.15	0.96	0.58	0.13	0.88	2.72	1.31
Discharge	m ³ /s	13.33	15.05	15.48	12.90	26.23	41.71	
²³⁸ U ^a	µg/L	0.05	0.04	0.08	0.15	0.27	0.48	0.25
²³⁴ U/ ²³⁸ U ^a		1.81	2.64	1.84	1.98	1.71	1.54	1.82
²³⁸ U natural	µg/L	0.05	0.04	0.08	0.15	0.19	0.27	0.17
²³⁴ U/ ²³⁸ U natural		1.81	2.64	1.84	1.98	2.01	1.96	2.02

^aAnalytical uncertainty ±10% (1σ standard deviation)**Fig. 4**

Chemical data for waters from the Corumbataí River basin (Santa Terezinha station) plotted on a standard Piper (1944) diagram

concentration in the analyzed rocks is dependent on the lithology, so that siltstones and claystones (Corumbataí, Tatuí and Irati Formations) have higher uranium concentration than sandstones (Pirambóia and Botucatu Formations), which is compatible with other reported values (Ivanovich and Harmon 1992). The weighted mean U concentration is 8.86 µg/g, whereas the mean weighted AR is 1.08, indicating near secular equilibrium between ²³⁸U and ²³⁴U isotopes at least over the last 1 million years.

Uranium in soils

Table 3 shows the uranium concentration and AR in the C horizon samples of the four soil profiles. The mean U concentration is 7.60 µg/g, where the lower value was found for the soil cover developed over the Pirambóia Formation. The mean ²³⁴U/²³⁸U activity ratio corresponded to 0.84, and indicated the preferential leaching of ²³⁴U relative to ²³⁸U, a typical result for soil/rocks subjected to recent weathering (Dooley and others 1966).

Weathering rate of the Corumbataí River basin

Table 4 summarizes the parameters necessary to perform the calculations at Corumbataí River basin. For this region, the determined *k* coefficient is equal to 0.245, implying that 24.5% of the available uranium in rocks is taken into solution during the weathering process. Using all the data given in Table 4 and applying the described formula, it is possible to obtain a value of 14.93 ton km⁻² year⁻¹ for *W*, which yields 0.0265 mm/year for *v*. These results show that one vertical meter of rock needs 38,000 years to be chemically weathered under present climatic conditions.

Discussion

The phosphate effect on U release

Palma-Silva (1999) monitored dissolved phosphate at the Corumbataí River basin and identified a large increase downstream from Rio Claro city, which was attributed to residential and industrial wastes discharged in the Rio Claro urban area. However, the total coliform data did not confirm this because a non-significant correlation was

Table 2
Uranium concentration ($\mu\text{g/g}$) and $^{234}\text{U}/^{238}\text{U}$ activity ratio in rocks of the Corumbataí River basin

Formation	Predominant rock type	Percentage of area	Number of samples	$^{238}\text{U}^a$ ($\mu\text{g/g}$)	$^{234}\text{U}/^{238}\text{U}^a$
Itararé	Diamictites	5	1	11.34	1.22
Itararé	Sandstones	5	1	3.99	0.91
Tatuí	Siltstones	4.5	1	11.22	0.81
Tatuí	Siltstones	4.5	1	14.71	0.73
Irati	Siltstones	3.5	1	15.50	1.10
Irati	Limestones	3.5	1	6.87	1.20
Corumbataí	Claystones	30.5	1	32.34	1.44
Corumbataí	Claystones	30.5	1	6.11	0.90
Corumbataí	Claystones	30.5	1	19.84	1.18
Corumbataí	Claystones	30.5	1	7.07	0.95
Pirambóia	Sandstones	31.5	1	5.69	1.14
Pirambóia	Sandstones	31.5	1	1.57	0.94
Pirambóia	Sandstones	31.5	1	6.18	1.05
Pirambóia	Sandstones	31.5	1	2.77	1.05
Botucatu	Sandstones	6.5	1	1.85	1.22
Botucatu	Sandstones	6.5	1	3.51	1.07
Serra Geral	Diabases	8	1	3.35	1.12
Basic rocks	Basic rocks	8	1	2.87	1.10
Rio Claro	Sandstones	9.5	1	4.50	1.13
Rio Claro	Sandstones	9.5	1	10.04	1.17
Bauru Group	Sandstones	1	–	–	–
Weighted mean				8.86	1.08

^aAnalytical uncertainty $\pm 10\%$ (1σ standard deviation)

Table 3
Mean uranium concentration ($\mu\text{g/g}$) and $^{234}\text{U}/^{238}\text{U}$ activity ratio in soils of the Corumbataí River basin

Horizon	Bed-rock	Depth (cm)	Description	$^{238}\text{U}^a$ ($\mu\text{g/g}$)	$^{234}\text{U}/^{238}\text{U}^a$
C	Pirambóia	>90	Podzol, yellow-red	2.86	0.71
C	Irati	>40/70	Podzol, dark red	9.67	0.81
C	Corumbataí	40/60–80	Podzol, dark red	8.51	0.94
C	Botucatu	60/80–100	Plintssol, light red	9.37	0.90
Mean				7.60	0.84

^aAnalytical uncertainty $\pm 10\%$ (1σ standard deviation)

Table 4
Parameters necessary to evaluate weathering rate in the Corumbataí River basin

E_R =uranium weighted mean content in rocks	8.86 $\mu\text{g/g}$
E_E =uranium weighted mean content in waters	0.17 $\mu\text{g/L}$
A_R =weighted mean $^{234}\text{U}/^{238}\text{U}$ activity ratio in rocks	1.08
A_E =weighted mean $^{234}\text{U}/^{238}\text{U}$ activity ratio in waters	2.02
A_S =mean $^{234}\text{U}/^{238}\text{U}$ activity ratio in soils	0.84
k =dissolution coefficient of uranium	0.20
ρ =mean density of rocks	2.3 g/cm^3
D =average monthly flow	26.4 m^3/s
S =surface of the basin	1,581 km^2

found with the phosphate data. Ferreira and others (1997) reported radiometric anomalies (^{238}U , ^{232}Th and ^{40}K) in soils developed on basic rocks (diabase sills) in the heavily cultivated Araras region (near the Corumbataí River

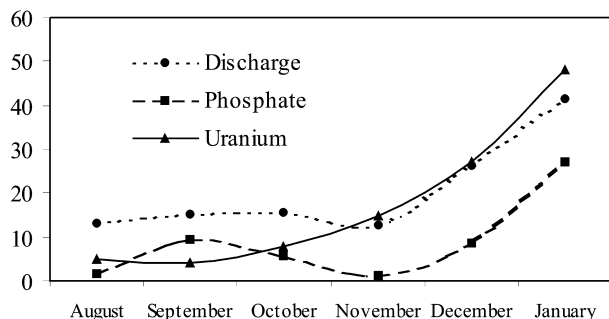
basin). These soils are known to normally contain low concentration of radionuclides and the radiometric anomalies were attributed to impurities in fertilizers. Long-continued application of U-bearing fertilizers can elevate the uranium concentration in fertilized soil profiles (Rothbaum and others 1979) and in irrigation runoff/drainage from fertilized lands (Spalding and Sackett 1972). Sugar cane is extensively cultivated in the Corumbataí River basin by industries that produce alcohol and sugar. Fertilizers are widely used in this type of agriculture, particularly in tropical regions, where weathering of soil nutrients is more intense. The phosphate rocks contain uranium (Altschuler and others 1958), which is incorporated in calcium phosphate minerals during their original deposition (Guzman 1992). The original uranium is largely retained in superphosphate and phosphoric acid during the manufacture of fertilizers produced from phosphate rocks (Guimond and Windham 1975; Roessler and others 1979). Most of the fertilizers used in the Corumbataí River basin come from the Araxá region (Minas Gerais), where the phosphate rocks typically have a U content of 180 ppm, whereas simple or concentrated (triple)

Table 5

Uranium concentration and AR in fertilizers (NPK) used in the Corumbataí River basin

Fertilizers	$^{238}\text{U}^a$ ($\mu\text{g/g}$)	$^{234}\text{U}/^{238}\text{U}^a$
NPK (5/25/25)	47.59	1.00
NPK (5/25/25)	47.73	1.00
Mean	47.66	1.00

^aAnalytical uncertainty $\pm 10\%$ (1σ standard deviation)

**Fig. 5**

Similarity of behavior among dissolved uranium ($\times 10^{-2}$ $\mu\text{g/L}$), discharge (m^3/s) and phosphate ($\times 10^{-1}$ mg/L) at Corumbataí River (Santa Terezinha station)

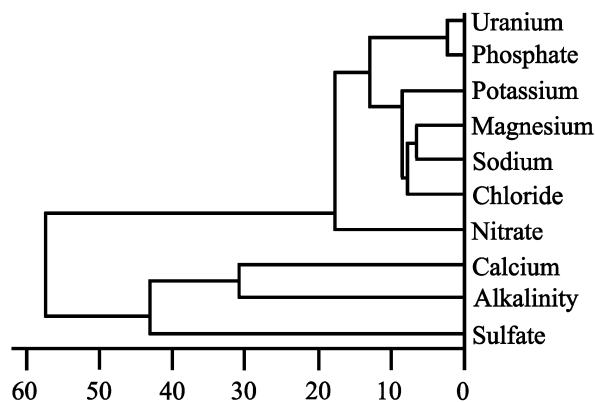
superphosphates reach up to 90–100 ppm (Paschoa and others 1984). They are of the NPK 5:25:25 type, i.e. 5% of nitrogen, 25% of phosphate and 25% of potassium (Fertiza 1986), exhibiting a U concentration of 47.7 ppm and AR of 1.00 ± 0.10 (Table 5).

Pfister and others (1976) reported that the uranium does not accumulate in soils, and that it is lost by leaching. Guimond (1978) considered that uranium is lost by erosion of the sediments together with the phosphate. Uranium is soluble under oxidizing conditions as uranyl ion, and in soils with low organic matter it can have the mobility equivalent to that of phosphate (Rothbaum and others 1979). Agricultural practices can elevate uranium concentration in shallow soils and co-existing water (Zielinski and others 1995), but in another study Zielinski and others (1997) attributed minimal impact of fertilizer-U compared to natural uranium leached from the local soils. The dissolved uranium concentration at Santa Terezinha station increased progressively from August 1998 (0.05 $\mu\text{g/L}$) to January 1999 (0.48 $\mu\text{g/L}$). Except for November 1998, the discharge of the Corumbataí River basin at the same site also increased continuously from 13.33 to 41.71 $\text{m}^3 \text{s}^{-1}$. The same occurred with dissolved phosphate, which increased from 0.15 to 2.72 mg/L . The monthly variation of these parameters from August 1998 to January 1999 is shown in Fig. 5. Thus, a significant positive correlation ($r=0.96$) exists between the uranium concentration and the river discharge. The most important uranyl complexes are formed with fluoride, phosphate and carbonate under acid, near-neutral and alkaline conditions, respectively (Langmuir 1978). Among these anions, there was a significant correlation only between dissolved

Table 6

Dissimilarity among chemical parameters of waters from the Corumbataí River (Santa Terezinha station)

Node	Group 1	Group 2	Dissimilarity	Objects in groups
1	Phosphate	Uranium	2.549	2
2	Sodium	Magnesium	6.571	2
3	Chloride	Node 2	8.040	3
4	Node 3	Potassium	8.683	4
5	Node 4	Node 1	13.049	6
6	Nitrate	Node 5	17.822	7
7	Alkalinity	Calcium	30.876	2
8	Sulfate	Node 7	43.005	3
9	Node 8	Node 6	57.275	10

**Fig. 6**

Dendrogram generated by cluster analysis applied to the ranked data for waters from the Corumbataí River basin (Santa Terezinha station). The unit of the x axis corresponds to Euclidean measure (UPGM)

uranium and phosphate ($r=0.84$) (Fig. 5), implying that the uranyl ions must be forming complexes with phosphate, a situation favored by their near-neutral conditions. Thus, these data suggest that the presence of dissolved phosphate affects the migration of the uranium into the waters of the Corumbataí River basin, and another way to confirm this is to use two different multivariate statistical approaches. The first methodology is the cluster analysis (CA) in *r-mode* (results cluster variables) which was performed using Ward's hierarchical agglomerative method (unweighted pair-group method, UPGM) and the squared Euclidean distance measured. CA was applied to the ranked data, with Table 6 presenting the dissimilarity among variables and Fig. 6 the obtained dendrogram. The results indicate that dissolved uranium and phosphate have the smaller dissimilarity (2.55), exhibiting a similar behavior. The second statistical treatment applied to the same ranked data set was the principal component analysis (PCA), which is an ordination method utilizing values and vectors from a variance-covariance matrix. The obtained results plotted in Fig. 7 indicate that dissolved uranium and phosphate have the same ordination and, therefore, a similar behavior. Thus, these two multivariate statistical approaches are also compatible with the evaluation performed by the use of the statistical correlation tests.

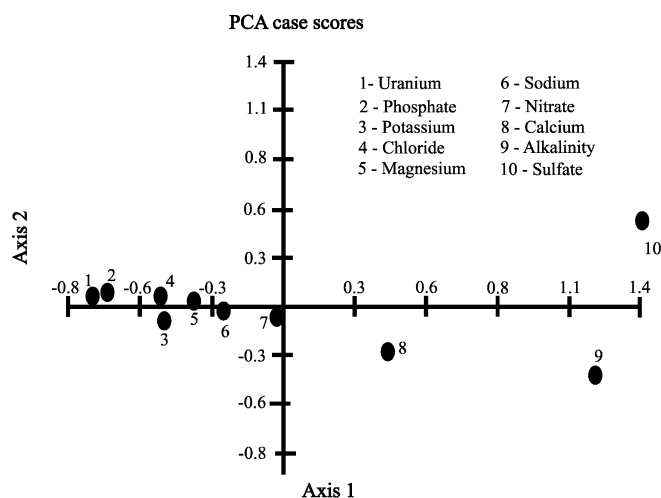


Fig. 7

Principal component analysis (PCA) utilizing data obtained for waters from the Corumbataí River basin (Santa Terezinha station)

These results reinforce what was suggested by Conceição and Bonotto (2000), indicating that the Corumbataí River can be receiving from laminar erosion (of the acid soils in the basin with low organic matter) large quantities of radionuclides, which are associated with phosphate fertilizers extensively used in agrichemical activities. In general, the cultivation of sugar cane starts in September/October, when about 28.5–30.5 g/m² of fertilizers is applied (Cotia Agricultural Cooperative 1991) and, in many areas, an additional 12.2 g/m² of superphosphate is applied. The higher concentrations of dissolved uranium and phosphate in the Corumbataí River (Santa Terezinha station) are more pronounced during wet periods when natural and fertilizer-derived U are more easily released from the soil cover. The presence of uranium and its radioactive daughters in added fertilizer may enhance the natural gamma radiation emitted by the soils (Menzel 1968; Mortvedt 1986; Guimond and Hardin 1989; Todorovskiy and Kulev 1993).

Fertilizer-derived U and the natural weathering rate

Non-natural inputs of uranium isotopes ²³⁸U and ²³⁴U in the drainage due to agrichemical activities can affect the modeling of weathering rates, because the equations used in the calculations are dependent on the concentration and ²³⁴U/²³⁸U activity ratio of dissolved uranium. The preferential release of ²³⁴U to the liquid phase is sustained during water–rock/soil/fertilizer interactions, and, thus, the AR values used in the calculation are not greatly affected by a fertilizer component. In contrast, the calculations are very sensitive to the value of the dissolved uranium concentration.

To properly correct such influence, it is necessary to know the amount of dissolved U from laminar erosion of soils enriched with phosphate fertilizers. It is expected there will be little influence of fertilizer-derived U during the dry season due to the poor U-leaching from soils. Thus, utilizing a weighted AR of 2.08, it is possible to obtain

$k=0.194$ for the period of August to November 1998, implying that 19.4% of available uranium in rocks is taken into solution during the weathering process. Because waters collected during the rainy season are certainly affected by fertilizer-derived U, higher k values are generated from dissolved U data for this period, i.e. 0.276 (December 1998) and 0.342 (January 1999), indicating that 70 and 57% of dissolved U is naturally originated in December 1998 and January 1999, respectively. Consequently, the fertilizer-derived U corresponds to 30 and 43%, respectively, in December 1998 and January 1999. Therefore, the natural dissolved U content should be 0.19 and 0.27 $\mu\text{g L}^{-1}$ during December 1998 and January 1999, respectively (Table 1).

The AR value of waters collected in the rainy season is also expected to be affected by fertilizer-derived U (Zielinski and others 2000), and if the equilibrium value of 1.00 ± 0.10 found for commercial phosphate fertilizer is taken into account (Table 5), then lower AR values should be obtained for samples collected during the rainy season, which effectively happens (see Table 1). Thus, one mass-balance equation can be written describing the complementary nature of the two phases (natural water and fertilizer-derived water):

$$A_M U_M = A_F U_F + A_N U_N \quad (5)$$

where U_M is uranium in mixed water; U_F is uranium in fertilizer-derived water; U_N is uranium in natural water; A_M is ²³⁴U/²³⁸U in mixed water; A_F is ²³⁴U/²³⁸U in fertilizer-derived water; and A_N is ²³⁴U/²³⁸U in natural water. The use of Eq. (5) allows the estimation of 2.01 and 1.96 as the natural AR, respectively, in December 1998 and January 1999 (Table 1). After evaluating the fertilizer effects on the calculations, it is possible to use the weighted mean uranium concentration and AR values from the whole period (Table 1), i.e. $U_E=0.17 \mu\text{g L}^{-1}$ instead of $0.25 \mu\text{g L}^{-1}$ and $A_E=2.02$ instead of 1.82. Now, the quantity of removed material in the Corumbataí River basin corresponds to 10.12 ton km⁻² year⁻¹, having a coefficient k of 0.204, which yields a velocity of alteration v of 0.022 mm/year, which implies that one vertical meter of rock needs 45,500 years to be weathered under present climatic conditions.

These results clearly show that the evaluation of the weathering rate based on the U-isotope disequilibrium method depends on any factor affecting the dissolved U concentration. The “fertilizer corrected” evaluation of the velocity of alteration (0.022 mm/year) is 55% lower than that reported by Moreira-Nordemann (1977, 1980) for the rocks of the Preto River basin, Brazil (0.04 mm/year). The Corumbataí River basin is large, contains many inhabitants, and exhibits several environmental problems related to residual, agricultural and industrial wastes; in contrast, the basin studied by Moreira-Nordemann (1977, 1980) is smaller and comparatively undeveloped. The rocks of the Preto River basin are metamorphic, more susceptible to erosion than the sedimentary rocks of the Corumbataí River basin (in general, metamorphic rocks have minerals that weather more easily than sedimentary rocks). Another dominant factor justifying

Table 7

Parameters necessary to evaluate weathering rate in the studied sub-basins

Parameter	Cabeças River sub-basin	Claro stream sub-basin
Area (km ²) ^a	119	253
²³⁸ U (μg/L) ^b	0.22	0.03
²³⁴ U/ ²³⁸ U ^b	1.58	4.33
Discharge (m ³ /s) ^a	1.61	2.82

^aBacci(1994)

^bSample collected on 08/13/1998

the different values is the great climatic variability of the two basins.

Weathering rate at two sub-basins

To investigate the effect of lithology and topography on weathering rates, two sub-basins of the Corumbataí River basin were chosen: Cabeças River and Claro stream. The Cabeças River sub-basin consists mainly of sandstones and the Claro stream sub-basin is composed predominantly of siltstones, basic rocks and claystones (Fig. 1). Table 7 reports the parameters necessary to obtain the weathering rates, i.e. area and discharge of each sub-basin, as well as the dissolved U content and AR during August 1998, which was the month less affected by fertilizers. The Cabeças River sub-basin has a smaller area and discharge than the Claro stream sub-basin. An inverse relationship is indicated between dissolved uranium concentration and AR. The uranium concentration and AR in rocks of the two sub-basins also must be known, and the weighted mean values in Table 8 were evaluated by graphically estimating the percentage of area covered by each formation in each sub-basin, and using uranium concentration for each formation from Table 2.

The calculated quantity of removed weathered material from the Claro stream sub-basin is 1.05 ton km⁻² year⁻¹ and from the Cabeças River sub-basin is 16.8 ton km⁻² year⁻¹. Utilizing these values and considering that sandstones covered 63% of the basin, it is possible to estimate the removal of 10.86 ton km⁻² year⁻¹ for the whole basin, which practically coincides with the “fertilizer corrected” evaluation (10.12 ton km⁻² year⁻¹). Equation (3) generated values of $k=0.08$ and 0.324 for the Ribeirão Claro

stream and Cabeças River sub-basins, respectively, implying that 8 and 32.4% of the uranium is taken into solution during the respective weathering processes. The velocity of weathering of the rocks determined by Eq. (2) yielded 0.0058 mm/year for the Claro stream sub-basin and 0.023 mm/year for the Cabeças River sub-basin. Therefore 172,000 and 40,000 years are necessary to weather 1 m of rock in present climatic conditions, respectively, at the Claro stream and Cabeças River sub-basins.

Wedepohl (1969), Gabelman (1977) and Krauskopf (1979) report that normally the uranium concentration is greater in siltstones and claystones than in sandstones. A higher mean weighted value of uranium concentration (9.99 μg/g) was found for rocks of the Claro stream sub-basin, consisting predominantly of siltstones and claystones. These rock types are less susceptible to weathering and leaching than coarse-grained sandstones of the Cabeças River sub-basin and this contributes to generating a lower value of dissolved uranium (Table 6) and coefficient of dissolution ($k=0.08$).

The Claro stream sub-basin has clayey-dominated soils, low average slope (6–12%), much protection due to the contour levels of the cultivated areas, and middle susceptibility to erosion (Bacci 1994), as confirmed by the weathering rate obtained in this paper. The Cabeças River sub-basin has more superficial sandy soils, higher slope (12–20%), not much protection due to the pasture, and high susceptibility to erosion (Bacci 1994), as also confirmed by the weathering rate obtained in this investigation. The sub-basin calculations indicate that much more material is supplied from the Cabeças River than from the Claro stream sub-basin. The Passa Cinco River sub-basin (Fig. 1) was not studied but has similar geology and similar susceptibility to erosion as that of the Cabeças River sub-basin.

Conclusions

The weathering rate of the rocks in the Corumbataí River basin, São Paulo state, Brazil, was estimated using the method of U-isotope disequilibrium. A value of 0.0265 mm/year indicated that it would take 38,000 years

Table 8

Uranium concentration and ²³⁴U/²³⁸U activity ratio in rocks of Claro stream and Cabeças River sub-basins

Sub-basin	Formation	Percentage of area	²³⁸ U (μg/g)	²³⁴ U/ ²³⁸ U
Claro stream	Corumbataí	40	16.34	1.12
	Rio Claro	25	7.27	1.15
	Serra Geral	20	3.35	1.11
	Pirambóia	10	4.05	1.05
	Irati	5	11.18	1.15
Weighted mean			9.99	1.12
Cabeças River	Pirambóia	60	4.05	1.05
	Botucatu	20	2.68	1.14
	Serra Geral	5	3.35	1.11
	Corumbataí	15	16.34	1.12
Weighted mean			5.57	1.08

to weather 1 m of rock under present climatic conditions. Significant correlations between uranium and phosphate ($r=0.84$), discharge and phosphate ($r=0.94$) and discharge and uranium ($r=0.96$), as well as multivariate statistical approaches, suggested that the presence of dissolved phosphate may be linked to the release of uranium in the basin. Fertilizers containing uranium and other impurities are used in the Corumbataí River basin in support of the important sugar cane agriculture. Estimates of the weathering rate that are based on assumed natural abundances of dissolved uranium may be affected by anthropogenic inputs of fertilizer-derived uranium, which may reach 43% in the wet period. After corrections, the weathering rate corresponded to 0.022 mm/year (45,500 years to weather 1 m of rock), demonstrating that the evaluation of the weathering rate utilizing the U-isotope disequilibrium method is affected by environmental factors acting in the Corumbataí River basin. The methodology was also useful for indicating relative differences in susceptibilities to erosion, related to different lithologies and topography.

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