J. Braz. Chem. Soc., Vol. 16, No. 2, 241-250, 2005.
Printed in Brazil - ©2005 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Influence of Domestic and Industrial Waste Discharges on Water Quality at Minas Gerais State, Brazil

Cláudio P. Jordão[*,a], *Madson de G. Pereira*[a], *Antônio T. Matos*[b] *and José L. Pereira*[a]

[a]*Departamento de Química and* [b]*Departamento de Engenharia Agrícola e Ambiental, Universidade Federal de Viçosa, 36570-000 Viçosa - MG, Brazil*

A contaminação aquática provinda de indústrias de processamento de caulim e de esgotos municipais tratados e não tratados, foi avaliada nos ribeirões Ubá e Vermelho, respectivamente, em Ubá e Vermelho Novo, em Minas Gerais. Com esta finalidade, amostras de água, material em suspensão e vegetais foram coletadas e analisadas. As análises envolveram a determinação da concentração de metais, nitrito, nitrato, cloreto, fosfato, demanda química de oxigênio e demanda bioquímica de oxigênio. O material em suspensão apresentou altas concentrações (em mg kg^{-1}) de Zn (2.400) e Fe (14.900), enquanto que a vegetação coletada nas proximidades dos ribeirões mostrou-se contaminada com Al (7.120). As concentrações de nitrito, nitrato e cloreto nas águas dos ribeirões apresentaram-se abaixo dos valores máximos estabelecidos pela Legislação Brasileira. Os valores de fosfato e demanda bioquímica de oxigênio excederam em 7 e 3 vezes, respectivamente, as concentrações máximas para águas superficiais de qualidade satisfatória.

The aquatic contamination from kaolin processing plants, as well as from untreated or inadequately treated municipal sewage, was evaluated in the Ubá Stream and Vermelho Stream, at the Minas Gerais State, Brazil. With this purpose, samples of water, suspended material and vegetation were collected and analysed. The analyses involved the determination of the concentration of metals, nitrite, nitrate, chloride, phosphate, chemical oxygen demand and biochemical oxygen demand. The suspended material showed high concentrations (in mg kg^{-1}) of Zn (2,400) and Fe (14,900), while the vegetation collected closed to the streams was heavily contaminated with Al (7,120). The concentrations of nitrite, nitrate and chloride in stream water were lower than the maximum values established by the Brazilian Environmental Standards. The phosphate and biochemical oxygen demand values exceeded 7 and 3 times respectively, the maximum concentrations for superficial water of satisfactory quality.

Keywords: stream water, heavy metal, sewage, kaolin

Introduction

The wastewater generated by kaolin processing industries, as well as by domestic activities, is generally released into streams at Ubá and Vermelho Novo at the Minas Gerais State, Brazil. The discarded materials contain potential toxic constituents, but no efforts to purify water have been conducted in the region. Efficient waste management practices that include potential hazard minimisation, recovery operations and treatment prior to stream emissions should be implemented. Particularly, heavy metals and organic compounds need to be controlled at the source to enable use of sewage, for instance, in irrigation or groundwater recharge. The lack of suitable waste treatment results in discharges of untreated or inadequately treated municipal and industrial sewage into aquatic environments, leading to deleterious health effects.[1]

The introduction of biodegradable organic matter in water systems decreases the level of dissolved oxygen.[2] Excessive growth of algae in lakes and reservoirs has been attributed to water contamination with nutrients, such as nitrogen or phosphorous.[3] The presence of nitrite and nitrate at high concentrations in drinking water can cause methemoglobinemia disease. This disease is more common in children and causes, among other symptoms, a cyanotic colour (bluish) in the skin due to blood alterations.[4] Watercourses that receive sewage also become sinks for anions such as chloride. The presence of heavy metals in stream water may also be harmful to human population through chronic poisoning.[1]

So far, no controls on emissions of pollutants to the environment have been set in the cities of Ubá and

---

* e-mail: jordao@ufv.br

Vermelho Novo at Minas Gerais State, Brazil, although the country established laws and regulations related to water resource conservation. In view of the above, the objective of this work is to evaluate the contamination of environmental samples caused by domestic (residential and commercial) and kaolin processing plant effluents discharges into the local streams.

Experimental

The study regions are located in southeastern Brazil and eastward to the Iron Quadrilateral Sector (Figure 1a). The sampling sites selected for this study were situated in Ubá and Vermelho Novo, as shown in Figures 1b and 1c, respectively.

The industrial activities in Ubá include metal furniture, leather tanning and kaolin processing plants. In Vermelho Novo, kaolin processing is also conducted where this mineral is mined.

Samples of suspended particle and riparian vegetation were analysed in order to obtain the concentration of Al, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, and Zn. The concentrations of nitrite, nitrate, phosphate and chloride were also evaluated in the stream water samples. In addition, aggregate organic constituents, *i.e.*, the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were determined in the collected water samples. The temperature of the watercourses was also determined. The data obtained were compared with the levels established by the Brazilian Environmental Standards.[5]

The Brazilian Environmental Standards establishes that fresh water resources are assorted according to the preponderant uses in four classes.[5] The stream water samples analysed in this study belong to Class 2. This group includes water for public supply after conventional treatment, recreation, irrigation or protection of aquatic biota.

Stream water samples were collected at about 10 cm below the surface in plastic bottles, previously rinsed with deionised water and further with surface water before filling. For nitrite and nitrate determinations, the plastic bottles were previously soaked in diluted hydrochloric acid and then rinsed with deionised water. For chloride determination, the plastic bottles were previously soaked in nitric acid and then rinsed with deionised water. For phosphate determination, the samples were collected in glass bottles in order to avoid adsorption on the walls of polyethylene containers. The glass bottles were previously soaked in diluted nitric acid and then rinsed with deionised water. The collected water samples were refrigerated at 4 °C and analysed within 24 hours. This is the corrected procedure for non-preserved samples.[6]

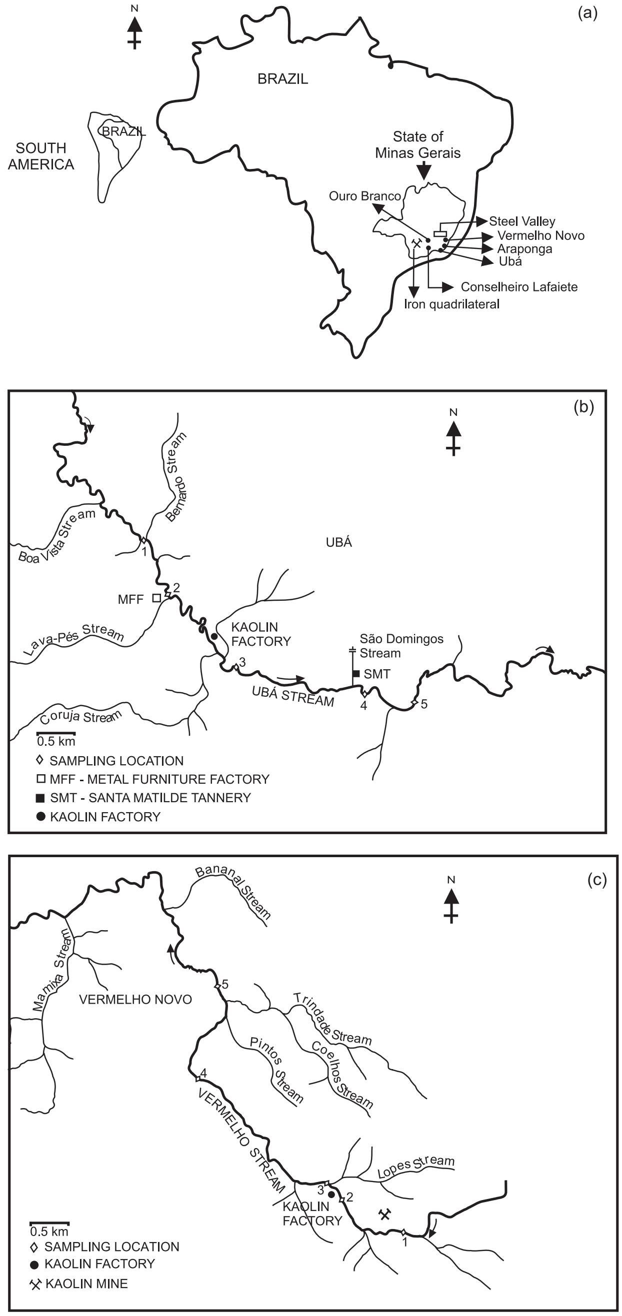

Figure 1. Maps of the areas studied showing: (a) State of Minas Gerais; (b) sampling sites in Ubá; (c) sampling sites in Vermelho Novo.

The suspended particles were obtained by filtering 500 mL of water using membrane filters of 0.45 μm pore size. The filters were previously analysed in respect to any metal contamination. When necessary, the water samples were first filtered through a No. 2 glass sinter to separate the coarse material. Filtration was performed under vacuum in a Buchner funnel. The filtration apparatus was washed with deionised water before use. The concentrations of nitrite and nitrate as well as the COD values were determined in the filtrates.

The membrane filters containing the residues were air dried during 48 h and digested with 10 mL of concentrated $HNO_3/HClO_4$ (1:1) mixture. The resultant solutions were diluted with deionised water to 25 mL and the concentrations of Al, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, and Zn were then determined.[7]

Grasses (*Brachiaria arrecta* and *Panicum rivulare*) were collected from the streambanks, stored in acid-washed plastic bags, transported to the laboratory at 5 ºC and washed with deionised water before metal analysis. The leaves were homogenised by cutting them into very small pieces with stainless-steel scissors, dried at 70 ºC for 48 h, ground in a blender and 5 g portions digested at 150 ºC with 10 mL of concentrated HNO_3 to near dryness. The samples were further digested at 150 ºC with 10 mL of concentrated HNO_3 and 5 mL of 30% (m/v) H_2O_2, and the mixtures evaporated to near dryness. The latter procedure was repeated four times and the resultant solutions diluted with deionised water to 25 mL. The concentrations of Al, Cd, Cr, Cu, Fe, Ni, Pb, and Zn were then measured in the solutions.[8]

The COD was determined in the water samples obtained by filtration through membrane filter using flasks with pre-measured reagents available commercially, following instructions described elsewhere.[6, 9] The sample was digested in a thermo-reactor for two hours at 148 ºC with a mixture of $K_2Cr_2O_7/H_2SO_4$. After cooling to room temperature, the COD was measured at 540 nm using a light path of 1 cm.

The BOD_5 determination was conducted in the water samples following the procedure described by Greenberg *et al.*[6] The test is based on the difference between the concentration of dissolved oxygen before and after incubating the samples at 20 ºC for 5 days. The pH values of the samples were corrected to between 6.5 and 7.5 with H_2SO_4 or NaOH, when necessary.

The assessment of the dissolved oxygen concentration in the samples to the determination of BOD was carried out using the iodometry method, modified by the addition of sodium azide. For this purpose, 2 mL of 0.12 mol L^{-1} $MnSO_4$ solution and 2 mL of an alkaline solution of sodium azide iodade were added to the incubation flask. After the precipitation of manganese hydroxide, the flasks were left to rest for 10 min, and then 2 mL of concentrated H_2SO_4 were added with vigorous agitation. A 100 mL aliquot of the resultant solution was titrated with 0.0125 mol L^{-1} Na_2SO_3 solution using a starch solution 0.5% (m/v) as indicator.

The nitrite concentration was determined by constructing a spectrophotometric calibration curve using the procedure of Greenberg *et al.*[6] For this purpose, a volume of 4 mL of the colour reagent was added to 95 mL of the water sample obtained by the water filtration through membrane filter. The reagent solution was obtained through the formation of a reddish purple azo dye produced at pH 2.0 by coupling diazoted sulfanilamide with N-(1-naphthyl)-ethilenediamine dihydrochloride. The absorbance was measured at 543 nm using a light path of 1 cm and 10 min after adding the colour reagent to the sample.

The nitrate concentration was determined by adding 1 mL of 1 mol L^{-1} HCl solution to 95 mL of the water sample obtained by the water filtration through membrane filter. The absorbance of the solution obtained was measured at 220 nm using a light path of 1 cm. The interference of NO_2^- ions and Cr (VI) was evaluated in this spectrophotometric method.[6]

The phosphate concentration in the water samples was determined by the ascorbic acid method. The sample was digested at 150ºC with 10 mL of concentrated $HNO_3/HClO_4$ (1:1) mixture. The colour reagent for phosphate determination as well as 2 mL of ascorbic acid solution (2%, m/v) was then added. The absorbance was measured at 725 nm using a light path of 1 cm.[10]

The chloride concentration of the water samples was determined by argentometric titration. The pH values of the samples were adjusted to the range of 6.5 to 9.0 with solutions of H_2SO_4 or NaOH as required. Turbid samples were first filtered through a membrane filter of 0.45 μm pore size.[6]

Samples from a clean spring (the Rochedo Site) in Araponga, close to the study area were investigated to obtain regional background levels. As examples of industrialised regions, also in the Minas Gerais State, samples from the Passagem Stream at Ouro Branco and from the Ventura Luís River at Conselheiro Lafaiete were also examined. These samples were analysed as described for the samples from Ubá and Vermelho Novo.

The concentrations of the aforementioned metals were measured with a Varian atomic absorption spectrophotometer (model SpectrAA 200), by direct aspiration of the solutions into an air-acetylene or nitrous oxide-acetylene flame. Background correction was used for Fe, Mn, Pb, Zn, Cd, Ni, Ca, and Mg determinations. The calibration blank was checked at the beginning and at the end of the analysis for each group of samples to certify that the instrument calibration had not drifted. To establish extraction efficiencies, our recurrent analyses of samples of Standard Sediments (National Institute of Standard & Technology no. 2704) gave the following values which are within the range of certified values: Zn = 447±4, Ni = 44.2±2.9, and Cu = 94.5±2.0 (in mg kg^{-1}); Al = 61.0±2 and Mg = 12.20±0.03 (in g kg^{-1}).

The water samples were previously filtered in a FABBE PRIMAR vacuum pump, model 341. The nitrite, nitrate and phosphate concentrations were determined in an UV-Visible HITACHI spectrophotometer, model U-2000. A MERCK photometer, model photometer sq 200, was used to obtain the COD values. A WTW BOD incubator, model TS603/3, was used. To the pH measurement a TECNOW pHmeter, model IRIS 7, was used. The temperature of the water samples was measured at sampling sites with a portable apparatus (QUIMIS, model Q-410).

Certified analytical grade reagents were used throughout. Nitric acid (65% m/v), HF 40% (m/v) and $HClO_4$ (70% m/v) were used for digestion, with maximum heavy metal contents reported by the supplier being (in μg mL^{-1}): Cd<0.01, Pb<0.02 and Ni<0.02. Blanks were run through all experiments to detect any contamination.

Results and Discussion

Suspended particle

Analysis of suspended particle provides data on the metal content and transport along watercourses, indicating that metal contamination can be found far from the emission sources.[11] Reports on the Acari-São João de Meriti River System in th Rio de Janeiro State, Brazil, have shown that the transport of heavy metals occurs via the particulate phase where mobile forms of metals prevail.[12] A large fraction of Fe, Zn and Cd was transported with the suspended particles in the Ubá Stream in Brazil, which runs near the vicinity of an electroplating industry.[13] The transport and availability of heavy metals in the Paraíba do Sul-Guandú River System in the Rio de Janeiro State, Brazil, have been studied. The authors found that the organic matter is the main vehicle in the transport of metals in the examined aquatic system.[14]

Metal concentrations in suspended particles from Ubá and Vermelho Novo are shown in Tables 1 and 2, respectively. Kaolin processing removes contaminants, mainly iron oxides that reduce its industrial application in paper manufactory. These impurities affect the colour and whiteness of paper.[15] The oxides can be removed by reducing Fe (III) to Fe (II), using metallic zinc. In addition to Zn and Fe, Al is also commonly present in effluents from kaolin factories, since it is a constituent of this mineral. The sample collected at site 3 in Ubá showed zinc concentrations in suspended particles higher than the global average. In the same locality, all sampling

Table 1. Metal concentration in suspended particles from Ubá

	Mean ± SD (mg kg^{-1}, dry wt.)[a]									
	Al	Ca	Cd	Cr	Cu	Fe	Mg	Ni	Pb	Zn
GASP[b]	-	-	1	100	100	-	-	-	150	350
Site										
PS[c]	4250±172	-	1.0±0.1	-	11	48800±4500	-	90.6±6.4	8.1±2.3	107±9
VLR[d]	2390±153	-	<0.4[e]	136±5	26.4±0.8	31.0±2.1	-	112±10	<0.5	187±29
1	1870±123	156±17	<0.4	7.2±1.5	1.8±0.2	7820±160	102±11	3.1±0.2	<0.5	36.0±3.3
2	1690±113	104±18	<0.4	1.9± 0.1	2.2±0.2	2840±160	31.2±6.0	2.6±0.1	<0.5	29.7±1.3
3	6670±270	327±21	<0.4	10.3±1.0	7.8±0.7	14900±1,240	111±7	3.4±0.1	<0.5	2400±145
4	766±15	177±31	<0.4	3.8±0.3	7.5±1.6	3640±252	27.0±2.2	8.4±1.7	<0.5	408±91
5	1140±128	178±23	<0.4	6.6±1.6	2.7±0.1	4410±125	38.9±4.0	1.3±0.3	<0.5	29.9±1.1

[a]Mean of three replicates ± standard deviation; [b]Global average for suspended particles (Ref. 7); [c]Passagem Stream (Ouro Branco); [d]Ventura Luis River Conselheiro Lafaiete); [e] Values preceded by < symbol indicate detection limits.

Table 2. Metal concentration in suspended particles from Vermelho Novo

	Mean ± SD (mg kg^{-1}, dry wt.)[a]									
	Al	Ca	Cd	Cr	Cu	Fe	Mg	Ni	Pb	Zn
GASP[b]	-	-	1	100	100	-	-	-	150	350
Site										
PS[c]	4250±172	-	1.0±0.1	-	11	48800±4500	-	90.6±6.4	8.±2.3	107±9
VLR[d]	2390±153	-	<0.4[e]	136±5	26.4±0.8	31.0±2.1	-	112±10	<0.5	187±29
1	1550±84	10.6±1.4	<0.4	18.5±2.9	8.0±0.8	2740±174	91.9±4.1	<0.5	<0.5	52.1±1.3
2	1502±111	9.5±1.8	<0.4	18.0±2.3	5.0±0.6	3740±200	85.6±10	<0.5	<0.5	16.0±1.4
3	4280±260	19.8±5.6	<0.4	22.0±2.1	5.9±1.3	12200±1130	59.8±3.2	<0.5	<0.5	535±45
4	3680±150	35.5±2.6	<0.4	17.9±0.8	3.1±0.1	4140±231	58.8±3.5	<0.5	<0.5	146±21
5	519±20	6.4±0.9	<0.4	17.9±1.3	0.6±0.1	1670±133	21.0±1.6	<0.5	<0.5	7.1±1.9

[a] Mean of three replicates ± standard deviation; [b]Global average for suspended particles (Ref. 7); [c] Passagem Stream (Ouro Branco); [d]Ventura Luis River (Conselheiro Lafaiete); [e] Values preceded by < symbol indicate detection limits.

sites presented Cd, Cr, Cu, and Pb concentrations below the global average. A similar situation was observed in Vermelho Novo, where Zn concentration reached up 535 mg kg^{-1}. Zinc concentrations in suspended particles from a kaolin dumping site in the Zona da Mata Mineira at Minas Gerais State, Brazil, were higher than the controls. The authors found the available Zn levels were potentially sufficient to cause problems to the local ecosystem.[16]

When zinc concentrations in suspended particles are compared with those of the industrialised cities of Ouro Branco and Conselheiro Lafaiete, elevated values are generally observed in sites close to kaolin processing plants. Thus, for example, site 3 at Ubá showed Zn concentration almost 22 times higher than the value observed in the Passagem Stream (Ouro Branco), and almost 13 times that of the Ventura Luis Stream (Conselheiro Lafaiete). The solid phase was very small in the water sample from the non-contaminated spring (Rochedo Site).

The wastewater treatment was not adequate to avoid metal discharges into the environment. The kaolin factory in Vermelho Novo, whose production reaches 120 tons of kaolin processed a month, discharges liquid effluents containing Zn, Al and Fe into the stream that runs in its vicinities. As expected, the suspended particles collected close to the kaolin processing plant discharges had higher Zn, Al and Fe concentrations.

Chromium concentrations in suspended particles collected at sites close to leather tanning factories were as high as 4,600 mg kg^{-1} in the Ubá Stream, and 11,000 mg kg^{-1} in the Patusca Stream, both in the Minas Gerais State.[17] In the present study, Cr concentration ranged from 3.8 to 10.3 mg kg^{-1} in Ubá, and from 17.9 to 22.0 mg kg^{-1}, in Vermelho Novo.

The importance of industrial effluents as a source of Cr and other metals for aquatic systems have been reported.[18,19] High average Cr concentration (80 mg kg^{-1}) in suspended particles from the Paraiba do Sul-Guandú River System has been attributed to the influence of the industrialised part of the study area.[14] Very high Cr concentrations (from 41 to 3,400 mg kg^{-1}) were also found in suspended particulate matter around the mouths of the Besós River and the pipeline of the Barcelona-Besós wastewater treatment plant in Spain.[20]

The Ca concentrations in suspended particles were higher in the samples from Ubá than those from Vermelho Novo. The elevated concentrations can be attributed to a greater load of contaminants in the Ubá Stream due to untreated domestic and industrial sewage, as compared to that of Vermelho Stream.

Vegetation

Tables 3 and 4 show the metal concentrations determined in the vegetation samples from Ubá and Vermelho Novo, respectively. Twenty percent of the samples collected in Ubá had a higher Al concentration than that of the Rochedo Spring. High concentrations of this element were also found in Vermelho Novo. Naturally, enhanced Al concentrations in flooded vegetation can be attributed to the discharge of industrial effluents. Aluminium is not a heavy metal, but it was included here due its toxicity to plant[21] and fish.[22]

Cadmium concentrations in the vegetation examined in this work were below the values commonly found in this material.[23] At the same time, the concentrations of this element in all vegetation samples examined in this work were lower than those reported for samples collected close to the Piracicaba River, which runs through the industrialised region of the Vale do Aço (Steel Valley) in the Minas Gerais State.[24] The vegetation from the Rochedo Spring showed cadmium concentration also below the detection limit (0.01 mg kg^{-1}).

Table 3. Metal concentration in plant tissue from Ubá

		Mean ± SD (mg kg^{-1}, dry wt.)[a]							
	Genera	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn
TMCP[b]		-	0.2 - 0.8	0.2 - 1	4 - 15	-	1	0.1 - 10	8 - 100
PR[c]	*Paspalum*	-	2.3 -12.7	3.1 - 17.1	3.4 - 38.7	-	1.1 - 6.4	5 - 31.3	12.7 - 82.9
Site									
RS[d]	*Eragrostis plana*	1180±55	<0.01[e]	5.4±1.1	2.8±0.3	619±33	2.9±0.3	<0.03	2.5±0.5
1	*Brachiaria arrecta*	593±71	<0.01	8.1±1.7	9.4±0.1	997±98	3.7±0.2	0.2±0.1	1.9±0.1
2	*Brachiaria arrecta*	1050±22	<0.01	6.5±0.4	4.9±0.3	2040±113	3.7±0.2	1.4±0.1	14.6±0.7
3	*Brachiaria arrecta*	925±2	<0.01	6.3±1.4	7.5±0.4	1330±126	3.3±0.2	1.5±0.1	233±23
4	*Brachiaria arrecta*	3000±45	<0.01	4.0±0.1	10.4±0.1	7360±5	2.4±0.1	3.6±0.1	609±4
5	*Brachiaria arrecta*	944±59	<0.01	4.3±0.1	10.4±1.0	1200±4	3.1±0.4	0.6±0.1	333±1

[a] Mean of three replicates ± standard deviation; [b] Typical metal concentration in plant (Ref. 21); [c] Piracicaba River (Ref. 22); [d] Rochedo Spring; [e] Values preceded by < symbol indicate detection limits.

Table 4. Metal concentration in plant tissue from Vermelho Novo

		Mean ± SD (mg kg^{-1}, dry wt.)[a]							
	Genera	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn
TMCP[b]		-	0.2 - 0.8	0.2 - 1	4 - 15	-	1	0.1 - 10	8 - 100
PR[c]	*Paspalum*	-	2.3 -12.7	3.1 - 17.1	3.4 - 38.7	-	1.1 - 6.4	5 - 31.3	12.7 - 82.9
Site									
RS[d]	*Eragrostis plana*	1180±55	<0.01[e]	5.4±1.1	2.8±0.3	619±33	2.9±0.3	<0.03	2.5± 0.5
1	*Brachiaria arrecta*	1230±355	<0.01	5.9±0.5	5.8±1.2	150±9	2.6±0.2	<0.03	2.1±0.1
2	*Brachiaria arrecta*	1440±102	<0.01	8.5±0.9	3.9±0.3	6840±100	3.5±0.5	<0.03	2.1±0.3
3	*Brachiaria arrecta*	3040±8 2	<0.01	11.3±1.8	2.8±0.3	4360±175	5.1±1.2	<0.03	1560±85
4	*Brachiaria arrecta*	7120±16	<0.01	18.7±4.2	6.9±0.8	11200±999	7.1±1.1	<0.03	914±43
5	*Panicum rivulare*	4400±134	<0.01	20.8±3.7	5.8±1.1	6030±34	14.0±2.4	<0.03	371±12

[a] Mean of three replicates ± standard deviation; [b] Typical metal concentration in plant (Ref. 21); [c] Piracicaba River (Ref. 22); [d] Rochedo Spring; [e] Values preceded by < symbol indicate detection limits.

High Cr concentrations were found when compared with those typically found in vegetation,[23] *i. e.*, from 0.2 to 1 mg kg^{-1}. The increase in Cr concentrations was surprising and should not be attributed to industrial effluent discharges from kaolin processing plants. The concentration of this metal in several sites was higher than that of the background level selected for comparison (the Rochedo Spring sample). The Cr concentrations observed in the study regions were, in general, close to those reported for vegetation collected in the surroundings of the Piracicaba River in the Vale do Aço.[24]

The Cu concentrations in *Brachiaria arrecta* are below the maximum value commonly reported for vegetation,[23] *i.e.*, 15 mg kg^{-1}. On the other hand, the concentration of this element at most sites examined were higher than the value observed in the vegetation from the Rochedo Spring. The vegetation from the Rochedo Spring site had only 619 mg Fe kg^{-1}. However, all plants examined in this work from the industrialised area of Ubá showed high Fe concentrations. The value in *Brachiaria arrecta* from site 4 of Vermelho Novo was very high (11,200 mg Fe kg^{-1}), showing again that the metal contamination along the streams can reach sites located far from the emission sources. It has been reported that levels of heavy metals increased in the downstream direction, particularly in roots of water hyacinth.[25]

As indicated by Tables 3 and 4, Ni concentrations ranged from 2.4 to 14 μg g^{-1} in *Brachiaria arrecta*. The toxicity of this element in plants is likely to occur only above 10 μg g^{-1} value.[26] The Ni background value for the Rochedo Spring site was 2.9 μg g^{-1}. Nickel contamination was also found in the vegetables collected in a mineralised site at the Minas Gerais State, Brazil. The authors reported nickel concentration as high as 7.9 mg kg^{-1}.[27]

The Pb concentration in the vegetation from the Rochedo Spring was below the detection limit (<0.03 mg kg^{-1}). The other sites examined gave values, which are within the range found elsewhere.[26,28,29]

The Zn concentrations found in vegetation show that effluent discharges from kaolin processing plants are contributing to the introduction of this element in the ecosystems examined. In fact, the vegetation collected up-stream the industries had lower Zn concentrations than those down-stream. While a high concentration (1,560 mg kg^{-1}) was reached at site 3 in Vermelho Novo, the highest value (609 mg kg^{-1}) in Ubá was observed at site 4. Concentration of this element as high as 2,330 mg kg^{-1} in *Brachiaria* sp. was observed at the Ubá Stream.[13] The Zn concentrations in vegetation collected near a kaolin mine site were also higher than the control values.[16]

Studies performed by Ho and Tai[30] have indicated that Zn is an essential element and its concentrations in non-contaminated plants are 100 μg g^{-1}. According to Alloway,[26] critical Zn concentrations in plants, *i.e.*, levels above which toxicity effects are likely to cause a 10% depression in plant yield, range from 100 to 900 μg g^{-1}.

Chemical Oxygen Demand

As expected, COD values for all water samples examined were higher than those obtained for BOD (Table 5), as the latter deals only with the oxidation of biodegradable organic matter.

The water sample collected in the Rochedo Spring showed a COD value of 2.0 mg L^{-1}. This is due to the presence of low concentrations of oxidable substances by $K_2Cr_2O_7$ in the waters of the Rochedo Spring. This value is lower than those of other rivers in Brazil,[31] such as the Jaguarí River (from 3 to 28 mg L^{-1}) and the Jundiaí River (from 3 to 77 mg L^{-1}). On the other hand, the samples from the industrialised areas analysed in this work showed COD values close to those rivers mentioned above.

The water from sampling site 3 of Ubá showed COD value higher than those from the other sites examined in this work. Site 3 is located close to the discharge point of

Table 5. Values of COD, BOD, nitrite, nitrate, phosphate and chloride of the collected waters[a]

		Site										
		RS[b]	Ubá					Vermelho Novo				
			1	2	3	4	5	1	2	3	4	5
Parameter	BES[c]											
COD (mg L^{-1})	-	2.0±0.3	21.7±1.7	43.3±3.8	105±13	63.3±3.1	34.7±4.5	39.0±2.6	52.0±4.6	54.0±3.0	59.0±2.1	69.0±3.4
BOD (mg L^{-1})	<5[d]	0.9±0.1	1.1±0.1	7.8±0.9	15.8±0.7	11.4±0.5	7.7±0.9	1.6±0.4	1.3±0.3	2.4±0.1	2.0±0.1	2.2±0.2
Nitrite (mg N L^{-1})	3300 <5[d]	<5	60.0±3.0	90.0±3.0	90.0±8.0	<5	<5	<5	3.0±0.2	<5	<5	
Nitrate (mg N L^{-1})	44300	2200±20	3080±170	4170±200	3450±12	5540±440	5440±23	3780±280	3730±99	2900±80	2310±210	2580±68
Phosphate (mg L^{-1})	25	<12	<12	<12	41.0±4.2	190±16	140±19	<12	13.0±1.2	16.0±0.1	<12	12.0±2.8
Chloride (mg L^{-1})	25000	1800±40	7600±600	9600±200	11700±600	17100±600	2130±60	4300±160	3300±290	4700±210	4700±320	5700±210

[a]Mean of three replicates ± standard deviation; [b]Rochedo Spring; [c]Brazilian Environmental Standards (Ref. 5); [d]Values preceded by < symbol indicate detection limits.

the kaolin processing plant. One may suppose that effluents from the factory are enriched with Fe (II), which is oxidable by acid solution of $K_2Cr_2O_7$.

In Vermelho Novo, there was an increase in the COD values from site 1 to 5. It might indicate the discharge of oxidable compounds up- and down-stream the emission points of industrial effluents. It was not visible significant amounts of suspended particle in the greyish waters from site 5 of this location. This site is located close to areas of corn, rice and coffee crops.

Biochemical Oxygen Demand

Table 5 shows the BOD values found in the water samples. The sample collected at the Rochedo Spring showed a BOD value below the limit for water quality Class 2 in Brazil,[5] *i.e.*, < 5 mg L^{-1}, indicating the absence of biodegradable organic pollutants. However, most sampling sites at Ubá showed BOD values in its waters above this value. The Jundiaí-Mirim River and the Corumbataí River in Brazil run through the industrialised regions of the São Paulo State. These rivers, selected for comparison purposes, presented high BOD values ranging from 1 to 24 and from 1 to 17 mg L^{-1}, respectively.[31] It is probably due to discharges containing untreated domestic wastes into its waters. In general, the polluted sites examined in this work had similar BOD values to those reported for the rivers of São Paulo.

Ubá and Vermelho Novo have, respectively, 77,159 and 8,000 inhabitants.[32] The higher BOD values found in Ubá were expected because the Ubá Stream receives a greater load of organic pollution due to untreated domestic sewage, as compared to the streams in Vermelho Novo.

Elevated BOD values (from 3.7 to 50.2 mg L^{-1}) have also been found in the Nile River, Egypt, where inferior water quality conditions were observed at the down-stream sampling stations.[33] Reports of the State Environmental Protection Agency on the water quality of the Arroio Pavuna River considered dramatic the situation of this river.[34] The Arroio Pavuna River carries most of the pollutants to the Jacarepaguá Lagoon, located in south Rio de Janeiro, Brazil. The Jacarepaguá Lagoon receives waste discharges from 235 factories, including metallurgical, chemical, textile, paper mills and food processing.[35] The BOD values found in this river range from 8.8 to 56 mg l^{-l}, while the dissolved oxygen and ammonia levels suggest that the lagoon is generally anaerobic.[34]

Nitrite

Table 5 shows the nitrite concentrations in the water samples. In the Rochedo Spring, its concentration was below the detection limit (<5 μg N L^{-1}). This result indicates the absence of biodegradable organic pollutants in the region. These pollutants can produce NO_2^- ion as an intermediary product when subjected to microbial oxidation.[36] The low concentration of nitrite, together with the reduced COD and BOD values (Table 5) indicate that the Rochedo Spring site is not affected by organic discharges.

The Piracicaba River flows through industrialised areas of the São Paulo State. It was reported nitrite concentrations ranging from 35.8 to 130 μg N L^{-1} in this river.[31] which are below the maximum limit established by the Brazilian Environmental Standards[5] for water quality Class 2. These low concentrations could be attributed to the fast conversion of NO_2^- to NO_3^- ions by nitrifying bacteria.[36] The nitrite concentrations in the water samples examined in this work were also below the maximum limit value established by the Brazilian Environmental Standards. However, the low concentrations cannot be attributed to the absence of pollution by organic biodegradable pollutants. The BOD values showed in Table 5 for the waters from Ubá sites were, in general, above the value established by the Brazilian Environmental Standards.[5] It means that these sites were contaminated with organic matter, which is capable of being decomposed by aerobic microorganisms. Thus, the reduced nitrite concentrations found in these sites, can be due to its relative easy conversion to nitrate ions.

Other areas of the Minas Gerais State show nitrite contamination. For example, it was reported that water samples from the Timotinho Stream, which were collected down-stream the effluent discharge point of a smelter, had higher nitrite concentration than the up-stream samples.[37] It indicates nitrite emissions at the collection period. Nitric acid is normally used to give a better finish to the steel in the scouring processing. On the other hand, experimental data on the evaluation of nitrite contamination in water reservoirs showed that its concentrations (in μg N L^{-1}) ranged from 3.3 to 23 in Porto Colômbia and Itumbiara, from 6 to 16 in Marimbondo, and from 1.0 to 7.9 in Furnas.[38]

Other rivers in Brazil receiving anthropogenic inputs are the Poxim River and the Grande River, where nitrite concentrations in its waters reached (in μg N L^{-1}) 333 and 51.5, respectively. While the former runs near an area of elevated industrial activity in the State of Sergipe,[39] the latter seems to suffer the effects of domestic waste discharges from two cities at the State of São Paulo.[40]

Nitrate

A preliminary experiment was conducted to evaluate the influence of nitrite and Cr (VI) in the nitrate determination. It was found that concentrations above 0.1 mg L^{-1} did affect the result of the nitrate analysis. Since their concentrations were below this value at all sites examined, it was not necessary to perform independent analysis to correct the nitrate concentrations.

The data from nitrate concentrations are presented in Table 5. All sites had nitrate values below the legal allowance for public health.[5] It was found in Ubá an increase in the nitrate concentration compared with that of site 1. This could be attributed to the organic matter present in domestic sewage discharges, since NO_3^- ions result from biodegradable organic matter containing nitrogen.[36]

The nitrate concentrations varying from 32.0 to 49.0 μg N L^{-1} in the Jundiaí-Mirim River and from 2.6 to 108 μg N L^{-1} in the Piracicaba River, were below the maximum value established by the water quality standards for Class 2 waters.[5] It was reported that water samples collected down-stream a smelter in the Timotinho Stream presented greater nitrate concentration than the up-stream samples.[37] It was reported nitrate concentration of 16.7 μg N L^{-1} in the Poxim River.[39] A particularly high input of this pollutant is recorded in the Grande River,[40] where nitrate concentration was almost 5 times higher than the maximum value established by the Brazilian Environmental Standards,[5] *i.e.*, 44,300 μg N L^{-1}.

In the Tubarão River at the Santa Catarina State in Brazil, the nitrate concentration varied from non-detected up to 50.8 μg N L^{-1}. This river flows through mining areas and waste deposits from charcoal processing. The relatively low nitrate concentration in the Tubarão River indicates that the region is not being contaminated with this pollutant.[41]

Concentrations of NO_3^- ions (in μg N L^{-1}) reported for water reservoirs at the Minas Gerais State varied from 5.6 to 31.4 in Porto Colômbia, from 2.9 to 37.2 in Itumbiara, from 7.0 to 27.8 in Marimbondo, and from 2.0 to 28.0 in Furnas.[38]

Total phosphate

The total phosphate concentrations obtained in the water samples are shown in Table 5. In the Rochedo Spring, the phosphorus concentration was below the detection limit (<12 μg L^{-1}). This result may be due to the absence of human activities, such as domestic sewage discharges. On the other hand, farming activities, which can affect the water of the spring examined, as many fertilisers contain the element phosphorus in their formulation, are also not developed in the region.[36]

The Piracicaba River presented phosphate concentration 6 times greater than the maximum limit established by the Brazilian Environmental Standards.[5,31] The high total phosphate concentrations in the waters of this river indicates contamination by effluents from domestic and industrial discharges, which may contain, among other substances, detergents with orthophosphate groups in their formulation. As shown in Table 5, 60% of the water samples from Ubá presented phosphate concentrations above the maximum limit value established by Brazilian Environmental Standards.[5] The deterioration of the water quality in the Warche River (Belgium) has also been observed where tributaries, sewage and dairy effluent flow into the river, inducing significant increase of phosphate, nitrite, nitrate and ammonium concentrations.[42]

Chloride

Chlorides present in natural waters come from natural sources such as mineral dissolution and also from anthropogenic inputs.[36] In the case of the water sample collected at the Rochedo Spring, the low chloride concentration can be attributed to natural inputs. As shown in Table 5, all the waters examined also showed concentrations of this ion below the maximum limit established by the Brazilian Environmental Standards.[5]

In Ubá, there was an increase in the chloride concentration from site 1 to 5. It might indicate the discharge of ions into the Ubá Stream from domestic sewage. A similar increase was also observed in the conductivity values at the same region.[43]

In Vermelho Novo, it was observed an increase of 21.28% in chloride concentration at site 5 as compared with that of site 3, which is located near the emission point of the kaolin processing plant. This fact was not surprising since the sample collected at site 5 in the Vermelho Stream is located down-stream the city of Vermelho Novo, which receive effluents from domestic activities.

Temperature

The temperature of the water samples collected at the autumn season ranged from 26.8 ºC to 31.0 ºC in Ubá and from 28.2 ºC to 32.2 ºC in Vermelho Novo.

Conclusions

The results of this work indicate that the streams examined receive effluents from domestic and industrial activities. Environmental samples (suspended particles and vegetation) show elevated concentrations of metals such as Zn, Al, Cr, and Fe. Stream water characteristics (phosphate concentrations as well as biochemical oxygen demand) are far from the established values for superficial water with satisfactory quality. However, the concentrations of nitrite, nitrate and chloride are, in general, within the background values.

Acknowledgements

We thank the Brazilian National Research Council (CNPq, Brazil) for the financial support.

References

1. Tavares, B. M.; Carvalho, F. M.; *Quim. Nova* **1992**, *15*, 147.
2. Harrison, R. M.; *Understanding our Environment: An Introduction to Environmental Chemistry and Pollution*, The Royal Society of Chemistry: London, 1995.
3. Moore, J. W.; Moore, E. A.; *Environmental Chemistry*, Academic Press, Inc.: London, 1976.
4. Dacach, N. G.; *Sistemas Urbanos de Água*, Livros Técnicos e Científicos: Rio de Janeiro, 1979.
5. Conselho Nacional do Meio Ambiente (CONAMA). *Estabelecer a Classificação das Águas Doces, Salobras e Salinas do Território Nacional*, Resolução CONAMA n° 20 de 18 de junho, Brasília, 1986, pp. 72-86.
6. Greenberg, A. E.; Clesceri, L. S.; Eaton, A. D.; *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association; Washington, 1992.
7. Torres, J. P. M.; *M.Sc. Dissertation*, Universidade Federal do Rio de Janeiro, Brazil, 1996.
8. Allan, J. E.; *Preparation of Agricultural Samples for Analysis by Atomic Absorption Spectrometry*. *S.1, S.I.S,* Varian Tectron bulletin 12, 1969.
9. Canadian Pulp and Paper Association; Standard Testing Methods: *Chemical. Oxygen Demand*, Montreal, 1980.
10. Dirceu, J. S.; *Análise de Alimentos* (*Métodos Químicos e Biológicos*), Imprensa Universitária da Universidade Federal de Viçosa: Viçosa, 1990.
11. Morrison, G. M.; Whei, M. C.; *Anal. Proc.* **1991,** *28*, 70.
12. Rego, V. S.; Pfeiffer, W. C.; Barcellos, C. C.; Rezende, C. E.; Malm, O.; *Environ. Technol.* **1993**, *14*, 167.
13. da Silva, A. C.; Jordão, C. P.; Pereira, J. L.; Viana, R. F.; *Rev. Esc. Minas Ouro Preto* **1999**, *52*, 94.
14. Malm, O.; Pfeiffer, W. C.; Fiszman, M.; Azcue, J. M; *Sci. Total Environ*. **1988**, *75*, 201.
15. Ampiam, S. G.; *Clays,* Bureau of Mines, Mineral Commodity Profiles: Whasington, 1979.
16. da Silva, A. C.; Mendonça, E. D.; Fontes, R. L. F.; de Marco, P; Ribeiro, F. P.; *Communic. Soil Plant Anal*. **2003**, *34*, 671.
17. Jordão, C. P.; Pereira, J. C.; Brune, W.; Pereira, J. L.; Braathen, P. C.; *Quim. Nova* **1999**, *22*, 47.
18. Carvalho, C. E. V.; Ovalle, A. R. C.; Rezende, C. E.; Molisani, M. M.; Salomão, M. S. M. B.; Lacerda, L. D.; *Environ. Geol.* **1999**, *37*, 297.
19. Hatje, V.; Bidone, E. D.; Maddock, J. L.; *Environ. Technol.* **1998**, *19*, 483.
20. Palanques, A.; *Environ. Monit. Assess.* **1994**, *85*, 205.
21. Fahl, J. L.; Carelli, M. L. C.; Deuber, R.; Nogueira, S. S. S.; Hiroche, R.; *Rev. Bras. Ci. Solo* **1982**, *6*, 203.
22. Heydron, K.; Alfassi, Z.; Damsgaard, E.; Rietz, B.; Solgaard, P.; *J. Radioanal. Nucl. Chem.* **1995**, *192*, 321.
23. Allaway, W. H.; *Adv. Agron.* **1968**, *20*, 235.
24. Jordão, C. P.; Pereira, J. C.; Brune, W.; Pereira, J. L.; Braathen, P. C.; *Environ. Technol.* **1996**, *17*, 489.
25. Klumpp, A.; Bauer, K; Franz-Gerstein, C.; de Menezes, M.; *Environ. Internat.* **2002**, *28*, 165.
26. Alloway, B. J.; *Heavy Metals in Soils*, Black Academic: New York, 1993.
27. Jordão, C. P.; Pereira, M. G.; Pereira, J. L.; Bellato, C. R.; *Anais Assoc. Bras. Quim.* **2000**, *49*, 31.
28. Jordão, C. P.; Pereira, J. L.; Jham, G. N.; Bellato, C. R.; *Environ. Technol.* **1999**, *20*, 489.

29. Albasel, N.; Cottenie, A.; *Water, Air, Soil Pollut*. **1985**, *24*, 103.
30. Ho, Y. B.; Tai, K. M.; *Environ. Pollut*. **1988**, *49*, 37.
31. Companhia de Tecnologia e Saneamneto Ambiental (CETESB). *Relatório de Qualidade de Águas Interiores do Estado de São Paulo 1998*, São Paulo, Brazil, 1999. (http;//www.cetesb.sp.gov.br).
32. Companhia de Processamento de Dados do Estado de Minas Gerais (PRODEMGE); *Projeto Cidades*, Belo Horizonte, Brazil, 1999. (http://www.cidades.mg.gov.br).
33. Abdelhamid, M. I.; Shaabandessouki, S. A.; Skulberg, O. M.; *Arch. Hydrobiol*. **1992**, *3*, 283.
34. Barcellos. C. C.; Fernandes, H. M.; Azevedo, H. L. P.; *Sci. Total Environ.* **1988**, *75*, 211.
35. Fundação Estadual de Engenharia do Meio Ambiente (FEEMA); *Quadro da Situação Ambiental da Bacia de Jacarepaguá*. Rio de Janeiro, Brazil, 1984. (http://www.feema.rj.gov.br, 10/09/2001).
36. Von Sperling, M.; *Introdução à Qualidade das Águas e ao Tratamento de Esgotos*, Segrac: Belo Horizonte, 1996.
37. Pires, C. K.; *M.Sc. Dissertation*, Universidade Federal de Viçosa, Brasil, 1999.
38. Sá Júnior, W. P.; *Estação de Hidrobiologia e Psicultura de Furnas*, DRM.O., São João da Barra, 1997. (http://www.furnas.gov.br, 10/09/2001).
39. Santos Filha, M. M.; Freitas, S. S.; Carvalho, J.; *Abstracts of the 22ª Reunial Anual da Sociedade Brasileira de Química*, Poços de Caldas, Brazil, 1999.
40. Mori, V.; Oliveira, G. F.; Bertotti, M.; Massaro, S.; *Abstracts of the 22ª Reunial Anual da Sociedade Brasileira de Química,* Poços de Caldas, Brazil, 1999.
41. Klug, M.; Lima, M. C.; Gotardo, H.; Bortoluzzi, I. P.; Dalmônico, A. L.; Martins, A.; *Abstracts of the 22ª Reunial Anual da Sociedade Brasileira de Química*, Poços de Caldas, Brazil, 1999.
42. Marneffe, Y.; Comblin, S.; Bussers, J. C.; Thome, J. P.; *Netherland J. Zool*. **1996**, *46*, 337.
43. Pereira, M. G.; *M.Sc. Dissertation*, Universidade Federal de Viçosa, Brasil, 2000.

Received: November 24, 2003
Published on the web: February 28, 2005