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Metal Contamination of Stream Waters
Under the Impact of Tanneries

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Abstract - This study evaluated the contamination of water samples from Cadeia and Feitoria rivers (Rio Grande do Sul State, Brazil), affected by tannery activities. From July 1999 to April 2000, four sampling campaigns were performed at ten sites in order to evaluate selected metals and ancillary physicochemical variables. Sample preservation and analyses followed recommendations of the *Standard Methods*. Factor analysis was used to obtain statistical indexes representing the contamination degree of waters evaluated. The information was summarized in two principal components. The first, which accounted for 50% of the total variance, was associated to a tannery contribution and generated a contamination index. Total, Suspended and Dissolved Solids, Dissolved Oxygen, Conductivity, Chromium, Manganese, Copper, Nickel, Sodium, Calcium, Potassium, and Magnesium were the well-correlated variables with this first component. The water quality decreased from headwaters up to mouth along both streams, but the most contaminated sites were located at the lower reach of Feitoria river (Ivoti and Lindolfo Collor cities), where tanneries are concentrated. After the entrainment of Feitoria waters (São Sebastião do Caí municipality), Cadeia river also presented an increased contamination degree. The application of statistical randomization tests highlighted these same sites as significantly distinct from the others. Water contamination also showed association to flow variations, and a poorer water quality was observed during the dry period (January). The second component, in which Iron, Aluminum, and Suspended Solids were the relevant variables, was loaded with 15% of the total variance. It was linked to natural events, since higher factor scores in this component were obtained during a period of increased water discharge (October), which caused re-suspension and entrainment of solid material to the rivers bed. As a final result of the study, sampling stations were classified according to the contamination degree, and graphically represented on a basin map, which synthesized the environmental diagnosis.

Keywords - Heavy metals; stream water; tannery.

INTRODUCTION

Processing hides and skins, together with the footwear sector, is a traditional activity in the State of Rio Grande do Sul, Brazil. During several decades, tanneries discharged considerable volumes of liquid effluents into some state rivers, while solid wastes were disposed directly on the land, often on the banks of rivers or in flood-prone areas (Krieger 2000). Even though over the last years specific laws and an improved effluent control have helped reduce pollutant emissions, many toxic compounds from the tanneries can still be observed in the waters and river sediments, representing a potential risk to the environment, with a direct or cumulative impact on the aquatic life and human health.

Leather manufacturing is one of the potentially most polluting branches of industry. Several substances are added to the skins until their transformation into leather, and they are present in the main tannery wastes. The use of chromium salts as tanning agents and their possible toxicity have been broadly discussed (Valaoras *et al*. 1991; Carré *et al*. 1994; Armienta *et al*. 1996; Jordão *et al*. 1997; Armienta *et al*. 2001; Aravindham *et al*. 2004). There is great concern to identify the metal in the liquid effluents, in the solid wastes deposited in the environment and in the tanned, finished leathers. However, there is a worldwide tendency to maintain the use of chromium predominantly in the tanneries,

because besides generating high-quality leather, the production process is rather favorable from the economic viewpoint (Guterres 1997).

In areas that are under the impact of tanneries, other metals can pollute the water resources, whether by addition during the production process or by contamination of the raw materials. Even after appropriate treatment of the tanning rejects, it is difficult to foresee the supporting capacity of the environment in relation to the accumulated discharge (Jordão *et al*. 1997). Thus, areas under the influence of tanneries should be carefully monitored, in order to prevent possible damage to the environment and to human health.

The characterization of an environmental compartment involves multiple measures for different objects, requiring the use of statistical techniques to identify associations between variables and highlight differences between samples of the universe investigated. Considering the diversity and the complexity of the information generated when evaluating water quality, besides the need for later integration of the results with other compartments, it is important to have mathematical tools available that could summarize the data, making them easier to interpret and to recognize tendencies. Factor analysis is a multivariate statistical technique that is often used to build environmental indexes in which a group of variables is substituted by a smaller set of hypothetical variables (or factors), which account for most of the variance of the original data. Applying factor analysis makes it possible to calculate a numerical value which combines a group of correlated variables on a common scale (Fachel 1976), synthesizing the environmental contamination at each sampling point on a given date. Besides providing flexibility to select variables and allowing an adaptation to existing data, factor analysis has shown satisfactory results when applied to performing environmental diagnoses (Haase *et al*. 1993; Teixeira *et al*. 2000; Rodrigues & Raya-Rodríguez 2003).

Even if certain patterns are identified in a set of environmental data, it should still be conjectured that any difference observed may have resulted uniquely from random processes. Based on a probability *P*, the hypothesis tests aim at interpreting the significance of similarities observed in a given sample of the universe under investigation. Considering that the data obtained in environmental studies do not always follow a theoretical distribution like the normal one, the tests of hypothesis by randomization have the advantage of generating *P* based on the data themselves. An iterative algorithm generates the repeated permutation of the data vectors and computes the statistical test that determines *P* (Pillar 2000). The foundations of the randomization tests applied here are described by Pillar & Orlóci (1996), with an application of the methodology to environmental data in Rodrigues *et al*. (2003).

Once the significant spatial and temporal variations have been identified, it is important to look for environmental descriptors that will support the interpretation of the results. In this sense, it is essential to understand the hydrologic regime, especially to identify the water surplus and deficit periods that normally control pollutant dilution and concentration (Laybauer 1995). Because of the input of toxic agents to the receiving body, the hydrodynamics configures scenarios of more or less critical water quality conditions, and exerts great influence on the supporting capacity of the environment (Hatje 1996).

This study evaluated the total and dissolved content of selected metals - cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), chromium (Cr), zinc (Zn), iron (Fe), manganese (Mn), aluminum (Al), and titanium (Ti), in the waters of Cadeia and Feitoria rivers (RS, Brazil), potentially under the impact of tanneries. In order to perform the environmental diagnosis, the river flows and the variables of temperature (T), dissolved oxygen (DO), pH, Eh, conductivity, total solids (TS), dissolved solids (DS), hexavalent chromium (Cr(VI)), sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) were also analyzed, applying descriptive and multivariate statistics to identify the tendencies in the set of data. The results were compared to the standards of the Brazilian law in force, and to typical values found in river environments. The determination of a statistical index of water contamination using factor analysis sought to condense and simplify the data so as to make them more intelligible to the public at large. As a tool to disseminate information, the sampling stations were identified on the basin map, according to the relative degree of water contamination.

STUDY AREA

The Cadeia and Feitoria rivers lie in the northeastern region of the state of Rio Grande do Sul, in southern Brazil, with a drainage area of appro

ximately 900 km². After their waters flow together, they discharge into the Caí, one of the main rivers forming the Guaíba hydrographic basin. The relief of the Cadeia and Feitoria rivers basin is quite varied. In the lower-lying parts of the basin, close to the mouth discharging into the Caí river, the relief is flat and slightly hilly, and towards the higher part there are regions with a markedly hilly relief and mountain slopes. The altitudes range from approximately 10 m in the Central Depression to approximately 800 m on the Plateau. According to the Von Koeppen classification, in the areas that lie at a higher altitude, the climate is the *Cfb* type, defined as temperate, with well-distributed rainfall throughout the year. In the lower region, the climate is *Cfa*, i.e., subtropical, with precipitation also well distributed throughout the year (FEPAM/FINEP, 2003).

The local geology consists of Serra Geral Formation, where basalt rocks predominate, Botucatu Formation, represented by sandstones of aeolian origin, and Tertiary sediments. According to FEPAM/FINEP (2003), the soils in the higher regions are mainly formed by basalt weathering, while at lower altitudes they derive from Botucatu sandstone. Generally they have good drainage, acid character, high oxide content (especially Fe), and variable depths, due to the relief. Because of the steep slope, soils are highly susceptible to erosion, and very stony in some places, especially on the Serra Geral slopes. About 60,000 inhabitants are distributed heterogeneously along the basin boundaries, 25,000 in the rural areas and 35,000 in urban areas. The region is characterized as based on a smallholding landownership structure. Labor is family–based, with subsistence farming, domestic animals raising and commercial production of vegetable and fruits. Only 2% of the territory correspond to urban areas, while 55% are occupied by native forests or reforestation areas, 6% by sparse woods, 28% by agricultural land and 5% by pastures.

Following the expansion of the hides and skins industry in the state, small and medium-sized tanneries settled in the region over time. They are currently the only relevant industrial activity in Cadeia/ Feitoria watershed. The eleven main tanneries established in the region process green or salted hides, until finished leather is obtained. The liquid effluents of these businesses undergo primary and secondary treatment to fulfill the legal specifications for punctual discharge into the receiving body of wa ter. Part of the leather and footwear industry center

of Rio Grande do Sul lies in the area of the study. This state accounts for 30% of the Brazilian foreign sales of leather, which were a total of US$1.4 billions in 2005 (Campos, 2006).

MATERIALS AND METHODS

Sampling and analyses of samples

Ten places were selected to collect surface water, which was done in July 1999, October 1999, January 2000 and April 2000, covering different hydrologic scenarios throughout the year. Due to the distance from anthropogenic sources, the references used were points FEI004 and CAD006. Points CAD003, CAD001 and FEI001 were chosen to measure discharge, performed with a current meter by technicians of the Instituto de Pesquisas Hidráulicas at Universidade Federal do Rio Grande do Sul. For the other sites, the discharge was estimated by the proportionality between drainage areas, taking sites CAD003 and FEI001 as the base for calculation in each river. Sampling followed procedures described by CETESB (1977) and Brazilian standard NBR9898 (ABNT 1987) for a total of 40 samples. The packaging, preservation and field analyses followed the recommendations of NBR 9898 (ABNT 1987) and APHA (1995).

Total metals, dissolved metals, total solids (TS), and suspended solids (SS) were analyzed in the laboratory of the environmental protection agency of Rio Grande do Sul (FEPAM). The content of dissolved solids (DS) was obtained by the difference between TS and SS. The analytic methods followed recommendations of APHA (1995), except for SS, determined according to the operational procedures for separating dissolved metals. The total metal content was evaluated in the whole samples, preserved during the collection with nitric acid (pH<2). The concentration of dissolved metals was analyzed in portions of the natural samples, which were vacuum-filtered through cellulose ester membranes (0.45 μm) and preserved at pH<2, right after arriving in the laboratory. The previously tared filters, containing the particulate material, were submitted to SS analysis. According to the element characteristics and after proper digestion procedures, the metal analyses were carried out by different techniques: a) Cd, Cr, Cu, Ni, and Zn - using a Jobin Yvon 38S inductively coupled plasma optical emission spectrometer, coupled to a CETAC U-50000 ultrasonic nebulizer, in order to attain lower detection limits; b)

Al - with a Varian 250-plus atomic absorption spectrometer, using a nitrous oxide-acetylene flame; c) Fe, Mn, and Pb - with a Varian 250-plus atomic absorption spectrometer, using an air-acetylene flame; d) Na, K, Ca, and Mg - by flame emission in a Varian 250-plus spectrometer; e) Hg - by cold vapor generation, using a Varian VGA-77 system coupled to a Varian 250-plus spectrometer; f) Ti - using a Varian UV-visible DMS-80 spectrometer, after complexation with hydrogen peroxide. Using a sample aliquot without acid preservation, Cr (VI) was analyzed in the filtrate, after complexation with diphenylcarbazide, using an UV/visible Varian DMS-80 spectrometer.

The samples were processed in duplicate, using ultrapurified water and Merck suprapur or p.a reagents. Each set of samples was accompanied by three blanks. Seeking to eliminate viscosity effects, reagent matched, multi-element standard solutions were used for calculating calibration curves. These solutions were prepared from certified standards Spex and Titrisol Merck (1,000 mg/L). The analytic accuracy was assessed with the simultaneous processing of standard-solutions prepared at the time of analysis, containing amounts of elements similar to those observed in real samples. The accuracy and precision of the analyses was satisfactory, in general obeying the criteria recommended by APHA (1992), i.e., recoveries between 80 and 120%, and differences between duplicates of up to 25% for concentrations 20 times lower than the detection limit (DL) and up to 10% for concentrations 20 times higher than the DL. DL was defined as three times the concentration equivalent to the background noise (APHA, 1995).

Data analysis

Preparation of the database and descriptive analysis of the variables

A data matrix with 39 columns (variables) and 40 lines (sample units) was organized. A sample unit represents the measures performed at each sampling site on a given date. Before the statistical analysis, variables with values not detected at all samplings – Cd, Cr (VI), Hg, and Pb were excluded. The other values not detected were substituted by half the DL. In a possible occurrence of impaired data, the gap was filled according to the behavior of the variable, considering mean values, correlation with other variables or spatial-temporal tendencies. Mean, standard deviation, maximum and minimum for each variable were calculated. The results were compared to the water quality standards established by Brazilian law (CONAMA 2005) and also to typical contents observed in stream waters (Bowen 1979).

Applying factor analysis

Aiming to determine a statistical index of water contamination, the factor analysis technique was applied to the data set, using the *Statistica for Windows 4.3* software with an option for principal components. The process began with the determination of the Pearson correlation matrix for the purpose of viewing associations and defining the relevant universe of variables. Next, the possibility of reducing the data and building a new set of synthetic variables or factors was explored. The correlation of the original variables with the extracted factors resulted in the factor loading matrix, in which the first component represents the best synthesis of the linear relationship exhibited by the data. Based on the factor loading matrix, the factor coefficients needed to calculate the factor scoreswere determined. The factor scores in relation to each factor were obtained from the following equation: $FS = c_1z_1 + c_2z_2 + ... + c_nz_n$, where FS is the factor score, calculated for each sample unit in relation to a given factor; c_n is the factor coefficient or weight of each variable in the composition of the factor score; and z_n is the standardized variable. In this study, it was not necessary to have an optional rotation in search of a solution with simpler factors that were easier to interpret. The factors retained for interpretation were selected using the *broken–stick* technique (Jackson 1993; Rodrigues *et al.* 2003) that compares eigenvalues observed for the real data with eigenvalues calculated for random data (Eq.1). The components whose eigenvalues are higher than those expected with random data are considered significant.

$$b_k = \sum_{i=k}^{p} \frac{1}{i} \, , \qquad \text{(Eq.1)}$$

b_k = magnitude of the eigenvalue for the k*th* component; p = number of variables; i = integer which varies from k to p.

Applying randomization tests

The MULTIV computer program (Pillar 2000) was used in the randomization tests in order to successively evaluate two null hypotheses (H_0): 1- On each sampling date, the observed data set is independent of its position along the rivers; 2- At each sampling site, the observed data set is independent of its position over time. The data matrix was submitted to a vectorial transformation (centering and normalization within variables) and a dissimilarity matrix was determined, computing Euclidean distances to compare sample units. Considering the original configuration of the data, the test criterion (λ) was calculated, corresponding to the sum of squares observed between groups (Q_b). After 10,000 random permutations of the data vectors, determining the respective sums of squares between the groups (Q_{b0}), the probability of the occurrence of the event was calculated as: $P (\lambda o \geq \lambda) = $ *Number of iterations* $\lambda_0 \geq \lambda$ / *Total number of iterations*. H_0 was accepted when P was superior to the level of significance (α), assumed as 0.05.

The sample units were stratified in homogeneous blocks. During the first test, the dates were fixed as blocks, and the significant differences between sampling sites were evaluated. During the second test the sites were fixed as blocks, evaluating whether the collection dates were significantly different from each other. Then, the contrasts between groups were evaluated. The contrasts are defined by positive and negative coefficients, which indicate the compared sample units. The probabilities $P(Q_{b0} \geq Q_b)$ were likewise generated and interpreted by comparison with arbitrated α (5%).

Mapping the results according to the degree of water contamination

For the purpose of obtaining a simple tool to disseminate the results, a water quality map was prepared, showing the sampling sites according to the relative degree of contamination. For this purpose, the factor scores on the first component were used, which best expressed the anthropogenic influence in the study area. The process began by calculating the quartiles of the first factor scores that were taken in the present study as water contamination indexes (*CI*). Using the criteria in Table 1 a new score was assigned to each sample unit, according to the magnitude of the factor score obtained. The number of times each site was located at a given interval was calculated, the value obtained was multiplied by the new score given, and the parcels were added up. Since there are four results per site, the largest possible number of points was 16 (worst environmental quality), and the minimum was 4 (best quality). Considering the interval with 12 units of variation, four classes of water quality were arbitrated (Tab. 2). The results of the classification were recorded on the river basin map, summarizing the information obtained in the environmental diagnosis. Adopting this procedure to classify collection points, instead of simply using the arithmetic mean of the scores, was intended to avoid the attenuation of possible seasonal water quality variations.

Table 1 - Quartile-based criterion to assign scores to the sample units.

Range of variation of the factor score in factor 1 (or contamination index, *CI*)	New score assigned
IC < Lower quartile	1
Lower quartile < CI < Median	2
Median > CI > Upper quartile	3
CI > Upper quartile	4

Table 2 - Classification of the collection sites, according to surface water quality.

Environmental quality	Number of points (X)	Classification
Best	$4 \leq X < 7$	❶
Upper mean	$7 \leq X < 10$	❷
Lower mean	$10 < X \leq 13$	❸
Worst	$13 < X \leq 16$	❹

RESULTS

Description of the behavior of variables

Tables 3 and 4 contain, respectively, the results of the study and a summary of the descriptive analysis of the data. At all collections undetected values were observed for Cd, Hg, Pb, and Cr (VI). The waters evaluated reflected oxidizing conditions, with generally high DO contents and markedly positive values of Eh. The pH remained close to neutrality and the Temperature fluctuations were compatible with the regional climate. In response to the increasing urban density and to the presence of sources of industrial and agricultural pollution, the DO contents diminished from the sources to the mouth, while Conductivity, DS, TS, Cr, Mn and Na presented the opposite behavior, with a more marked deviation

from the baseline in Feitoria river. On the contrary of DO, the highest Conductivity, DS and TS values occurred in January 2000 (dry period) and the lowest in October 1999, under conditions of greater water availability, revealing discharge-dependent processes for the dilution of materials. Considering the typical values for stream waters, DS contents were mostly below the world average (100 mg/L), and similar to the South-American rivers (55 mg/L), which reflected a relatively high degree of water dilution (Berner & Berne, 1987).

On the contrary of Ca, which was below the world average, relatatively high mean concentrations of Al, Cr, Fe, Mn and Na were found. It is in fact expected that subtropical rivers have waters with high Al and Fe content. Due to intense leaching processes, the suspended particles originate in soils enriched with these scarcely soluble elements (Berner & Berner 1987). In the waters evaluated, the high Fe concentrations could stem from the weathering of altered basalts of Serra Geral Formation and the ferruginous matrix of the Botucatu sandstones (Baisch 1994). Fine-grained Fe and Mn oxides/hydroxides are typical products of basalt alterations, and potential carriers of metals into the water environment (Förstner & Wittmann 1981).

The analysis of the ratio of Na to Ca content showed a value close to the unit at the points with less influence from anthropogenic sources (0.8 at sites FEI004 and FEI003 of Feitoria river and 1.1 in the CAD006-CAD003 section of Cadeia river). On the other hand, this quocient attained a value of 1.7 at the most contaminated points of Cadeia river (CAD001 and CAD002) and 2.4 in the area that suffers the greatest impact of the tanneries (points FEI002 and FEI001 of Feitoria river), which revealed an important input of anthropogenic Na at these sites. Cr and Mn presented comparatively high contents at these same sampling sites, which also indicated a potential contribution of the anthropogenic activities developed in the region.

Table 5 ranks the metals analyzed as to the mean dissolved percentage. Na, Ca, Mg and K, which occurred in an almost entirely dissolved form (>90%), showed the highest potential for export by the waters in the downstream direction. Zn, Cu and Mn, with an intermediary dissolved fraction (about 50%), also showed a considerable mobility and potential bioavailability, while Ti, Ni, Fe and Al (<30%) showed less mobility, less potential bioavailability and a higher tendency to retention within the limits of the area of study. The dissolved parcel of

Cr was located between the low and medium magnitude intervals (39%).

The experimental results of the present study indicated the occurrence of the trivalent form of Cr in the water samples, since the concentrations of Cr(VI) were located below the detection limit of the analytic method (<10 μg/L). Cr (VI) is highly toxic and water soluble, while Cr(III) is essential for the organisms and presents a lower migration potential, because it tends to precipitate as a scarcely soluble hydroxide or form chelates with organic molecules adsorbed to mineral surfaces (Armienta *et al*. 1996; Wittbrodt & Palmer 1996). When Cr is introduced into the environment, its speciation and its solubility are strongly conditioned by the pH and Eh conditions. Several reducing agents can convert Cr (VI) into Cr(III), as Fe(II) (Buerge & Hug 1997), organic matter (Wittbrodt & Palmer 1996; Vitale *et al*. 1997; Nakayasu *et al*. 1999) and sulfide (Vitale *et al.* 1997). According to many studies, aerobic and anaerobic bacteria are also able to mediate the reduction of Cr (VI) (Marsh & McInerney, 2001). On the other hand, there are indications that the only natural oxidants of Cr (III) in the surface environment are the Mn oxides, which are widely distributed in the suspended material of stream waters, also occurring as nodules and coating of particles in soils and sediments (Kim *et al*., 2002). The oxidation of Cr (III) to Cr(VI) in the aqueous medium is very complex and depends on the conjunction of various factors, unlikely to be observed in natural streams.

Regarding the proportion of SS and DS in the waters evaluated, against expectations, the dissolved materials content was always higher, even in the period of higher discharges. Although many studies use the 0.45 μm membrane to separate the suspended material, the filtrate may contain a high amount of colloidal matter (0.001-1 μm in diameter) and not truly dissolved forms (Hart & Hines 1995).

Save for a few exceptions, the results were satisfactory when compared to the current standards of class 2 waters. Point FE1001 presented a DO value that disagrees with the limit (3.2 mg/L in January 2000), and concentrations that are incompatible with the Total Mn standard (121 μg/L in July 1999 and 156 μg/L in January 2000). In October 1999, point CAD001 also presented a value of Total Mn above the limit (109 μg/L) and point CAD002 presented a pH 5.8 below the legal level. Almost all the Dissolved Al values and a large part of the Dissolved Fe concentrations went higher than the quality standards. High Al and Fe contents are continuously ob-

Table 3 - Results obtained in the evaluation of water quality in the Cadeia and Feitoria rivers.

SITE	DATE	Temp °C	DO mg/L	pH	Eh mV	Cond µS/cm	TS mg/L	SS mg/L	DS mg/L	CuT µg/L	CuD µg/L	NiT µg/L	NiD µg/L	CrT µg/L	CrD µg/L	ZnT µg/L	ZnD µg/L	MnT µg/L	MnD µg/L	FeT mg/L	FeD mg/L	AlT mg/L	AlD mg/L	TiT mg/L	TiD mg/L	NaT mg/L	NaD mg/L	KT mg/L	KD mg/L	CaT mg/L	CaD mg/L	MgT mg/L	MgD mg/L
FEI04	Jul99	15.2	9.4	7.3	207	46.7	44	2.2	41.8	0.6	0.4	0.2	<0.2	0.7	0.5	7.1	2.5	5	4	0.36	0.14	0.20	0.18	<0.10	<0.10	2.85	2.81	1.03	0.94	3.51	3.34	1.02	0.95
	Oct99	18.0	11.9	6.1	310	40.8	49	5.9	43.1	0.8	0.3	<0.2	<0.2	1.1	0.5	11.1	2.8	12	<4	0.70	0.25	0.58	0.31	<0.10	<0.10	2.58	2.58	0.85	0.84	3.44	3.40	1.49	1.41
	Jan00	20.8	9.8	7.2	218	43.8	58	6.9	51.1	1.1	0.7	<0.2	<0.2	0.8	0.4	11.8	3.6	16	6	0.65	0.24	0.80	0.28	<0.10	<0.10	2.73	2.73	1.52	1.27	4.55	4.43	1.4	1.36
	Apr00	18.2	10.2	6.3	163	36.6	61	3.9	57.1	0.6	0.5	0.9	<0.2	0.7	<0.2	6.4	4.9	9	<4	0.53	0.19	0.67	0.26	<0.10	<0.10	2.80	2.70	0.92	0.91	2.99	2.99	1.67	1.61
FEI03	Jul99	14.5	9.8	7.7	341	89.0	63	5.7	57.3	1.2	0.5	0.6	0.4	4.7	3.6	4	2.9	30	20	0.69	0.26	0.69	0.28	<0.10	<0.10	5.11	5.11	1.62	1.48	6.35	6.03	1.85	1.72
	Oct99	19.1	10.3	6.3	140	61.0	74	32.5	41.5	2.5	0.4	1.1	0.2	4.4	1.3	9.7	5.4	32	15	1.84	0.31	2.29	0.30	0.34	<0.10	3.51	3.50	1.07	1.00	5.20	5.08	2.10	1.85
	Jan00	22.8	8.3	7.4	245	77.6	79	25.5	53.5	3.5	1.4	2.3	<0.2	7.2	1.0	9.6	3.2	71	36	2.43	0.37	2.39	0.39	<0.10	<0.10	4.71	4.71	2.08	1.67	6.80	6.80	1.96	1.84
	Apr00	18.1	10.2	6.3	195	58.5	78	6.8	71.2	1.2	0.6	1.2	0.2	1.5	0.8	7.3	2.5	22	14	0.90	0.34	1.03	0.37	0.15	<0.10	4.40	4.40	1.22	1.16	5.12	4.86	2.58	2.56
FEI02	Jul99	14.1	8.9	6.9	194	206	151	10.4	141	2.9	1.1	0.8	0.2	29.6	13.8	11.6	5.9	53	61	1.05	0.34	2.34	0.73	0.25	0.12	23.7	23.5	2.12	1.94	9.71	9.23	2.71	2.52
	Oct99	16.5	9.1	6.1	215	89.6	92	23.7	68.3	2.5	2.3	2.1	0.3	29.9	12.9	6.0	3.3	86	31	2.06	0.63	1.52	0.14	0.20	<0.10	6.49	6.49	1.14	1.08	6.32	6.32	2.04	2.04
	Jan00	21.8	6.4	7.0	193	260	164	22.8	141	1.3	0.8	1.0	<0.2	37.6	4.8	6.0	4.7	72	56	1.35	0.18	1.22	0.44	<0.10	<0.10	31.5	31.5	2.81	2.52	12.4	11.3	2.38	2.37
	Apr00	18.0	10.0	7.5	173	144	140	7.8	132	5.4	5.2	1.5	<0.2	6.6	1.6	13.1	10.5	56	72	1.20	0.21	2.20	0.15	0.36	0.23	19.5	18.5	1.56	1.49	8.64	8.43	3.51	3.48
FEI01	Jul99	15.2	6.5	7.2	186	347	212	26.0	186	3.9	1.2	3.0	1.5	29.4	13	20.1	10.2	121	91	2.10	0.27	3.43	0.92	0.23	0.23	42.4	40.5	2.71	2.47	13.4	12.7	3.27	3.04
	Oct99	19.0	9.5	6.4	125	91.0	105	27.0	78	6.2	1.8	1.8	0.3	16.8	8.1	46	8.4	74	38	3.47	0.76	2.42	0.13	0.18	0.13	6.42	6.42	1.20	1.08	7.23	6.45	2.21	1.69
	Jan00	22.9	3.2	6.6	218	542	318	47.0	271	1.1	1.0	0.5	0.4	43.7	26.9	12.0	5.6	156	122	2.30	0.28	1.63	0.37	<0.10	<0.10	67.9	66.1	3.66	3.04	18.5	18.3	3.50	3.26
	Apr00	18.2	8.4	6.9	214	227	174	14.5	160	0.6	0.3	0.6	0.3	19.6	5.0	6.2	2.5	68	55	1.47	0.38	1.35	<0.10	<0.10	<0.10	32.0	30.0	1.72	1.66	9.48	8.95	4.12	3.8
CAD06	Jul99	13.4	9.6	7.5	251	33.0	24	17.6	6.5	0.9	0.6	0.5	0.2	0.6	0.2	13	6.2	35	10	1.57	0.16	0.52	<0.10	<0.10	<0.10	2.13	2.03	1.36	1.24	2.26	2.15	0.56	0.52
	Oct99	14.5	11.9	6.1	260	31.4	35	6.81	28.2	1.5	0.4	<0.2	0.2	0.4	<0.2	11.5	5.7	16	6	0.59	0.13	0.60	0.14	0.20	<0.10	2.14	2.16	1.09	1.08	1.89	1.86	0.89	0.80
	Jan00	18.3	9.7	6.6	206	27.0	42	4.8	37.2	2.6	0.5	0.3	<0.2	0.4	0.2	3.0	2.4	20	12	0.72	0.30	0.60	0.15	<0.10	<0.10	2.09	2.09	1.40	1.17	1.96	1.48	0.72	0.67
	Apr00	16.0	10.8	6.4	162	27.0	51	7.1	43.9	1.8	0.3	0.6	<0.2	0.3	<0.2	6.3	4.6	10	6	0.59	0.16	0.70	<0.10	<0.10	<0.10	2.20	2.10	1.22	1.14	2.07	2.07	1.12	1.08
CAD05	Jul99	13.5	10.4	7.4	265	49.7	48	2.8	45.2	0.9	0.6	0.2	0.2	0.5	0.4	38.3	7.0	9	4	0.47	0.21	0.36	0.14	<0.10	<0.10	3.17	2.97	1.40	1.28	3.73	3.54	1.07	0.99
	Oct99	15.5	10.9	6.0	245	45.6	57	6.9	50.1	1.5	0.9	0.3	<0.2	1.5	0.9	35.5	5.0	17	7	1.04	0.54	1.30	0.82	0.13	<0.10	2.54	2.56	1.60	1.49	4.25	4.13	1.47	1.45
	Jan00	22.1	8.9	6.1	211	41.1	68	30.0	38.0	2.6	1.4	0.9	<0.2	1.2	0.2	7.7	2.3	30	8	2.92	0.34	2.85	0.32	0.15	<0.10	2.72	2.72	1.98	1.70	4.25	4.25	1.19	1.05
	Apr00	17.2	10.6	6.5	240	41.1	75	7.0	68.0	1.8	0.9	1.0	<0.2	0.8	<0.2	16.8	12.2	23	6	1.18	0.33	1.45	0.50	0.21	<0.10	2.80	2.80	1.56	1.38	3.24	3.21	1.66	1.6
CAD04	Jul99	13.8	9.7	7.5	250	22.8	86	3.6	82.4	1.4	1.1	0.3	0.3	3.5	2.7	9.8	7.9	14	9	0.63	0.31	0.60	0.22	0.31	<0.10	9.49	9.49	1.84	1.68	5.60	5.32	1.8	1.67
	Oct99	17.1	10.5	6.9	250	58.5	79	13.0	66.0	2.3	0.8	0.6	<0.2	1.8	0.8	7.4	4.9	27	8	1.54	0.45	1.45	0.57	0.18	<0.10	3.73	3.73	1.37	1.28	4.90	4.80	1.85	1.71
	Jan00	21.8	8.4	7.0	192	61.8	76	21.1	54.9	2.2	1.3	0.5	<0.2	2.8	0.5	3.7	2.1	24	10	1.67	0.39	1.87	0.47	0.21	0.13	4.77	4.77	1.62	1.60	5.05	5.00	1.45	1.43
	Apr00	16.7	9.2	6.3	230	57.4	86	11.2	74.8	1.1	0.6	0.9	<0.2	1.5	0.7	7.1	7.1	16	6	1.09	0.40	1.30	0.42	<0.10	<0.10	5.80	5.80	1.55	1.50	4.17	4.17	2.15	2.06
CAD03	Jul99	14.3	10.8	7.3	211	81.4	67	6.1	60.9	1.2	0.7	0.4	<0.2	2.5	1.1	12.3	8.2	35	8	0.69	0.27	0.65	0.21	0.12	<0.10	5.73	5.47	1.64	1.50	5.05	4.80	1.80	1.67
	Oct99	17.0	10.8	7.1	220	59.6	79	14.8	64.2	1.4	1.0	1.1	<0.2	3.3	1.7	15.5	8.5	25	10	1.95	0.76	2.28	1.45	0.20	<0.10	3.48	3.44	1.37	1.32	5.43	5.18	1.92	1.84
	Jan00	23.3	8.2	6.5	198	113	104	7.3	96.7	7.9	1.6	0.4	<0.2	2.9	1.0	9.3	3.2	22	12	0.93	0.29	0.99	0.24	0.15	<0.10	10.4	10.4	2.15	1.83	6.95	5.50	1.97	1.92
	Apr00	17.3	9.7	6.5	216	57.2	88	8.7	79.3	0.9	0.4	0.4	<0.2	2.2	0.3	7.7	7.3	31	9	1.17	0.41	1.43	0.51	0.15	<0.10	5.2	5.2	1.48	1.47	4.35	4.35	2.45	2.07
CAD02	Jul99	15.4	8.6	7.3	204	167	111	7.2	104	1.3	0.8	0.4	0.3	6.0	3.4	14.3	3.1	47	25	0.76	0.27	0.69	0.20	0.31	0.20	17.8	17.6	2.05	1.51	7.57	7.14	2.48	2.12
	Oct99	19.1	10.1	5.8	250	70.1	91	22.5	68.5	2.8	0.8	1.8	<0.2	12.1	5.6	12.5	3.2	61	14	2.53	0.57	1.62	0.72	0.20	<0.10	4.43	4.43	1.71	1.28	6.53	5.83	2.17	1.99
	Jan00	23.1	8.3	7.4	220	129	93	8.2	84.8	4.2	1.3	1.8	<0.2	9.2	1.6	13.5	6.0	30	24	1.81	0.21	1.86	0.13	<0.10	<0.10	10.0	9.95	2.58	2.14	10.6	9.78	2.75	2.70
	Apr00	19.1	10.9	6.8	146	86.1	106	11.4	94.6	1.1	0.7	0.4	<0.2	6.1	1.9	6.3	5.1	70	14	1.16	0.33	1.14	0.39	<0.10	<0.10	10.0	9.70	1.70	1.61	5.44	5.3	3.08	2.30
CAD01	Jul99	15.7	7.8	7.2	168	183	129	14.5	115	1.5	0.8	0.8	0.5	15.4	6.8	14.2	7.2	109	39	1.44	0.32	1.21	0.39	0.20	<0.10	18.6	18.4	2.19	2.00	8.68	8.25	2.61	2.43
	Oct99	19.0	9.3	6.4	300	81.0	111	52.5	58.5	3.9	1.7	2.2	<0.2	14.0	6.3	5.4	4.9	74	52	3.64	0.87	2.97	0.93	0.39	<0.10	5.76	5.76	1.52	1.46	6.68	5.98	1.87	1.35
	Jan00	25.6	6.4	6.9	240	221	143	7.6	135	2.2	1.6	0.3	<0.2	6.4	3.1	12.2	3.0	57	54	0.84	0.28	0.57	0.16	0.15	<0.10	23.0	22.8	2.79	2.19	11.2	9.30	3.00	2.96
	Apr00	20.4	9.6	6.6	156	133	144	16.1	128	1.6	0.9	1.5	0.3	8.2	1.6	3.0	3.0	57	33	1.69	0.38	1.72	0.45	0.15	<0.10	17.1	16.5	1.82	1.80	6.79	6.75	3.16	2.99
Detection limit										0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	4	4	0.01	0.01	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2

Table 4 - Results of applying descriptive statistics and comparison with quality standards.

| VARIABLE | FEITORIA RIVER (n=16) | | | | CADEIA RIVER (n=24) | | | | REFERENCE SITE | | DETECTION LIMIT | TYPICAL CONTENT STREAMS [a] | COMPARISON WITH CONAMA-357 [b] | | |
| | | | | | | | | | | | | | QUALITY STANDARD | OUT OF STANDARD | |
	MEAN	MAX.	MIN.	STD. DEV.	MEAN	MAX.	MIN.	STD. DEV.	FEITORIA (mean)	CADEIA (mean)				Feitoria	Cadeia
Temp. (°C)	18.3	22.9	14.1	2.8	17.9	25.6	13.4	3.4	18.1	15.6					
DO (mg/L O$_2$)	8.9	11.9	3.2	2.1	9.6	11.9	6.4	1.3	10.3	10.5			>5	1	0
pH	6.8	7.7	6.1	0.5	6.8	7.5	5.8	0.5	6.7	6.6			6.0 - 9.0	0	1
Eh (mV)	208	341	125	55	220	300	146	38	225	220					
Cond. (µS/cm)	147	542	36.6	140	78.2	221	22.8	53.2	42	29.6					
TS (mg/L)	116	318	44	73.8	83	144	24	31.8	53	38					
SS (mg/L)	16.8	47	2.15	12.8	12.9	52.5	2.75	10.7	4.69	9.05					
DS (mg/L)	99.6	271	41.5	65.9	70.2	135	6.45	31.4	48.3	28.9			500		
Cd T (µg/L)	<0.2	<0.2	<0.2	0	<0.2	<0.2	<0.2	0	<0.2	<0.2	0.2	0.1	1	0	0
Cd D (µg/L)	<0.2	<0.2	<0.2	0	<0.2	<0.2	<0.2	0	<0.2	<0.2	0.2			0	0
Cu T (µg/L)	2.3	6.2	0.6	1.7	2.0	7.9	0.6	1.6	0.8	0.8	0.2	3	9	0	0
Cu D (µg/L)	1.2	5.2	0.3	1.2	0.9	1.7	<0.2	0.4	0.5	0.4	0.2				
Pb T (µg/L)	<16	<16	<16	0	<16	<16	<16	0	<16	<16	16	3	10	(c)	(c)
Pb D (µg/L)	<16	<16	<16	0	<16	<16	<16	0	<16	<16	16				
Ni T (µg/L)	1.2	3	<0.2	0.8	0.7	2.3	<0.2	0.6	0.3	0.3	0.2	0.5	25	0	0
Ni D (µg/L)	0.3	1.5	<0.2	0.3	0.2	0.5	<0.2	0.1	<0.2	<0.2	0.2				
Cr T (µg/L)	14.6	43.7	0.7	14.9	4.3	15.4	0.3	4.5	0.8	0.4	0.2	1	50	0	0
Cr D (µg/L)	5.9	26.9	<0.2	7.4	1.7	6.8	<0.2	2	0.4	<0.2	0.2				
Cr(VI) (µg/L)	<10	<10	<10	0	<10	<10	<10	0	<10	<10	10				
Hg T (µg/L)	<0.2	<0.2	<0.2	0	<0.2	<0.2	<0.2	0	<0.2	<0.2	0.2	0.1	0.2	0	0
Hg D (µg/L)	<0.2	<0.2	<0.2	0	<0.2	<0.2	<0.2	0	<0.2	<0.2	0.2				
Zn T (µg/L)	11.8	46	4	9.9	12.1	38.3	3	8.6	9.1	8.4	0.2	15	180	0	0
Zn D (µg/L)	5.2	10.5	2.5	2.7	5.4	12.2	2.1	2.5	3.5	4.2	0.2				
Mn T (µg/L)	56	156	5	42	34	109	9	24	11	20	4	8	100	2	1
Mn D (µg/L)	39	122	<4	35	16	54	4	14	<4	9	4				
Fe T (mg/L)	1.44	3.47	0.36	0.86	1.36	3.64	0.47	0.79	0.56	0.87	0.01	0.5	0.3	6	14
Fe D (mg/L)	0.31	0.76	0.14	0.16	0.36	0.87	0.13	0.18	0.21	0.19	0.01				
Al T (mg/L)	1.53	3.43	0.2	0.9	1.31	2.97	0.36	0.7	0.56	0.79	0.1	0.3	0.1	16	21
Al D (mg/L)	0.34	0.92	0.13	0.22	0.39	1.45	<0.10	0.33	0.26	0.1	0.1				
Ti T (mg/L)	0.14	0.36	<0.10	0.11	0.16	0.39	<0.10	0.09	<0.10	<0.10	0.1	0.005			
Ti D (mg/L)	<0.10	0.23	<0.10	<0.10	<0.10	0.2	<0.10	0.03	<0.10	<0.10	0.1				
Na T (mg/L)	16.2	67.9	2.58	18.9	7.3	23	2.09	6.08	2.74	2.1	0.1	6			
Na D (mg/L)	15.7	66.1	2.58	18.3	7.2	22.8	2.03	6	2.71	2.04	0.1				
K T (mg/L)	1.7	3.66	0.85	0.79	1.71	2.79	1.09	0.41	1.08	1.27	0.1	2.2			
K D (mg/L)	1.53	3.04	0.84	0.66	1.53	2.19	1.08	0.3	0.99	1.16	0.1				
Ca T (mg/L)	7.73	18.5	2.99	4.2	5.36	11.2	1.89	2.48	3.62	2.04	0.2	15			
Ca D (mg/L)	7.41	18.3	2.99	4.05	5.01	9.78	1.48	2.17	3.54	1.89	0.2				
Mg T (mg/L)	2.36	4.12	1.02	0.87	1.88	3.16	0.56	0.74	1.4	0.82	0.2	4			
Mg D (mg/L)	2.22	3.8	0.95	0.83	1.72	2.99	0.52	0.68	1.33	0.77	0.2				

(a) Bowen (1979); (b) CONAMA (2005) - class 2; (c) Detection limit above the quality standard

served by FEPAM while monitoring the quality of the river waters in Rio Grande do Sul, indicating that the national quality standards established for these parameters probably do not agree with the regional geochemical characteristics. Al is generally not considered a typical contaminant in surface waters, but there is evidence of its connection to human diseases like bone problems, Alzheimer's disease and encephalopathy in patients on dialysis (Florence 1982; Nriagu, 1988; ATSDR 1999). The physicochemical characteristics and bioavailability of Al are influenced by the water pH. In pH<4, large amounts of Al may be dissolved, but between 4 and 9, as in the present case, solubility is limited to < 1 mg/L (Brownlow 1972).

Multivariate analysis

Factor analysis

Once factor analysis had been applied, the *broken-stick* test indicated that the first two factors should be retained for interpretation (Fig. 1). These factors, observed in the factor loading matrix (Table 6), together accounted for approximately 66% of the variance of the original data, and they were characterized by sets of well-correlated variables, that can be associated with common sources of metals.

The first factor presented an eigenvalue of 16.1, with 50.3% of the total variance. The variables more closely correlated with this factor were DO, Conductivity, TS, SS, DS, Total and Dissolved Cu, Dissolved Ni, Total and Dissolved Mn, Total and Dissolved Cr, Total and Dissolved Na, Total and Dissolved Ca, Total and Dissolved K, and Total and Dissolved Mg. High values of most of these variables could be linked to the contribution from the tanneries that are the main sources of punctual pollution in the region. On the contrary of the other variables, DO was negatively correlated with the first factor, since its content in water diminishes when contamination increases. The second factor presented an eigenvalue of 4.9, containing 15.4% of the total variance. The variables that were well correlated with this factor were Total and Dissolved Al, Total and Dissolved Fe, Total Ni and SS, which would indicate a natural influence on water quality, probably because of erosion and silting processes

which occur during high discharge periods in the rivers. Due to the predominance of basalt rocks in the basin, high concentrations of Al and Fe are expected in the waters, especially during heavy rainfall events. The variable SS was distributed between the two factors (correlations around 0.6), and its behavior was associated both with an anthropogenic contribution and with natural events which promote the mobilization of solids by river waters.

Table 7 presents the factor scores obtained by the sample units regarding factors 1 and 2. Since they reflected the contribution of anthropogenic sources, the scores in the first factor were interpreted as water contamination indexes (*CI*). The spatial and temporal variation of these indexes is illustrated in figure 2, in which a contamination gradient can be observed from the sources to the mouth in both rivers. Figure 3 presents the mean of contamination indexes at each collection point, highlighting in dark colors the sites where there is lower environmental quality. The following hierarchy of contamination was observed: CAD006 < FEI004 < CAD005 < CAD004 < CAD003 < FEI003 < CAD002 < CAD001 < FEI002 < FEI001. The most contaminated points were located in Feitoria river, showing the contribution of the municipalities of Lindolfo Collor (FEI001) and Ivoti (FEI002), which concentrate most of the hides and skins industries. Cadeia river was most affected environmentally at point CAD001, in São Sebastão do Caí, after the inflow of the Feitoria river waters. Point CAD002 also showed a certain degree of water contamination, probably due to the influence of a tannery established in São José do Hortêncio city.

Among the variables investigated, T, pH and Eh, besides Zn and Ti in the total and dissolved form had low correlations with the factors that could be interpreted, and were less relevant to characterize the study area. On the other hand, the variables that are highly correlated with the first factor indicated contamination that was characteristic of tannery activity. Tanning operations typically originate wastewaters with high contents of TS, both in dissolved form, due to the different types of salts used in the productive processes, or suspended, because of the presence of hairs, greases, fibers and other undesirable materials. Even after treatment, the liquid effluent

Table 5 - Percentage wise fraction of the elements analyzed observed in the dissolved fraction, considering all collection sites (mean of 40 results)

	Ti	Ni	Fe	Al	Cr	Mn	Cu	Zn	K	Mg	Ca	Na
Mean (%)	8	17	28	29	39	51	53	54	91	93	95	99
Std. Dev.	21	27	11	18	22	22	21	25	7	6	6	2

discharged into water may still contain residual amounts of SS or DS, which mark the sites that suffer the impact. Another characteristic of tannery influence is the reduction of DO in the receiving waters, due to the possible presence of biodegradable materials (Schünemann *et al*. 1983). The gradual increase observed in the contents of Cr and Mn along both rivers also appeared to signal the growing influence of the hides and skins industries. Given that salts of Cr (III) are commonly used as tanning agents, this element can be considered the source signature of the tanneries in the aquatic environment. Mn sulfate can be used as a catalyst in the oxidation of sulfides that should be eliminated

during the treatment of tannery effluents. On the other hand, the increased salt contents of waters affected by tanneries may generate a cation competition for binding sites at solid particles, and thus promote a migration of natural metals with high potential availability (such as Mn) from the river sediments to the overlying waters (WHO, 2004).

Table 6 - Factor loading matrix.

VARIABLE	FACTOR 1	FACTOR 2
Temperature	0.372	0.148
Dissolved Oxygen	-0.861	0.174
pH	0.108	-0.480
Eh	-0.203	-0.005
Conductivity	0.945	-0.256
Total Solids	0.963	-0.117
Suspended Solids	0.606	0.627
Dissolved Solids	0.914	-0.275
Total Copper	0.665	0.333
Dissolved Copper	0.742	0.070
Total Nickel	0.489	0.655
Dissolved Nickel	0.618	0.038
Total Manganese	0.931	0.163
Dissolved Manganese	0.949	-0.076
Total Chromium	0.865	0.035
Dissolved Chromium	0.840	0.078
Total Aluminum	0.490	0.794
Dissolved Aluminum	-0.050	0.787
Total Iron	0.472	0.814
Dissolved Iron	0.113	0.871
Total Zinc	0.405	0.334
Dissolved Zinc	0.410	0.221
Total Sodium	0.926	-0.304
Dissolved Sodium	0.927	-0.304
Total Calcium	0.961	-0.144
Dissolved Calcium	0.965	-0.140
Total Potassium	0.833	-0.273
Dissolved Potassium	0.852	-0.272
Total Magnesium	0.735	-0.139
Dissolved Magnesium	0.726	-0.211
Total Titanium	0.368	0.460
Dissolved Titanium	0.542	-0.177
Variance Explanation	16.1	4.9
Proportion of Total (%)	50.3	15.4

Table 7 -Factor scores which, in the first factor, correspond to water contamination indexes (IC).

| Sample unit	Local	Date	Factor 1	Factor 2
1	FEI004	Jul 99	-1.063	-1.003
2		Oct 99	-1.079	-0.295
3		Jan 00	-0.732	-0.612
4		Apr 00	-0.905	-0.394
5	FEI003	Jul 99	-0.474	-0.889
6		Oct 99	-0.281	1.006
7		Jan 00	0.202	0.729
8		Apr 00	-0.486	-0.086
9	FEI002	Jul 99	0.923	-0.904
10		Oct 99	0.251	1.581
11		Jan 00	1.356	-1.047
12		Apr 00	0.395	-0.792
13	FEI001	Jul 99	2.671	-0.331
14		Oct 99	0.518	2.700
15		Jan 00	3.778	-0.455
16		Apr 00	0.938	-0.721
17	CAD006	Jul 99	-0.958	-0.129
18		Oct 99	-1.162	-0.470
19		Jan 00	-0.994	-0.396
20		Apr 00	-1.053	-0.609
21	CAD005	Jul 99	-0.960	-0.931
22		Oct 99	-0.595	0.729
23		Jan 00	-0.171	1.349
24		Apr 00	-0.628	0.214
25	CAD004	Jul 99	-0.268	-0.504
26		Oct 99	-0.447	0.451
27		Jan 00	-0.201	0.366
28		Apr 00	-0.500	-0.104
29	CAD003	Jul 99	-0.577	-0.700
30		Oct 99	-0.277	1.654
31		Jan 00	0.182	-0.164
32		Apr 00	-0.471	-0.003
33	CAD002	Jul 99	0.262	-0.978
34		Oct 99	-0.041	1.370
35		Jan 00	0.521	-0.386
36		Apr 00	-0.164	-0.365
37	CAD001	Jul 99	0.613	-0.640
38		Oct 99	0.607	2.970
39		Jan 00	0.848	-1.279
40		Apr 00	0.426	0.071
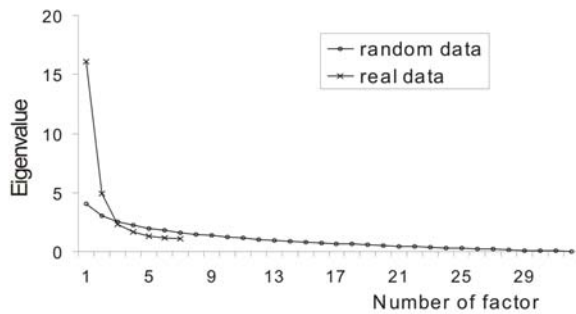
Figure 1 -Eigenvalues resulting from factor analysis of observed and random data, containing 32 variables and 40 sample units (*broken stick* method).
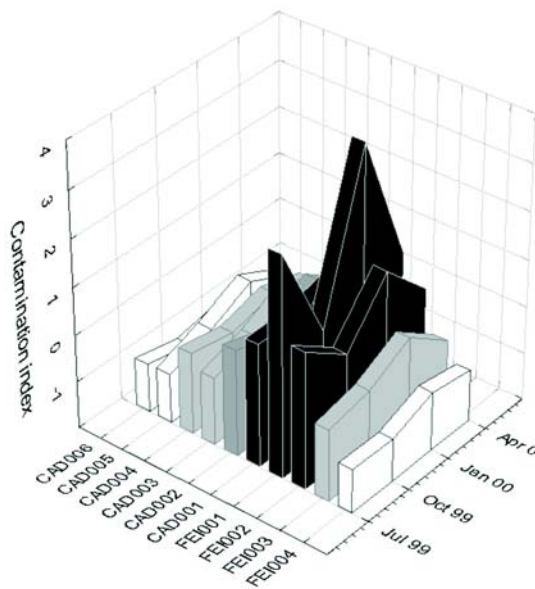

Figure 2 -Spatial and temporal variation of scores in factor 1, arbitrated as water contamination indexes (*IC*).
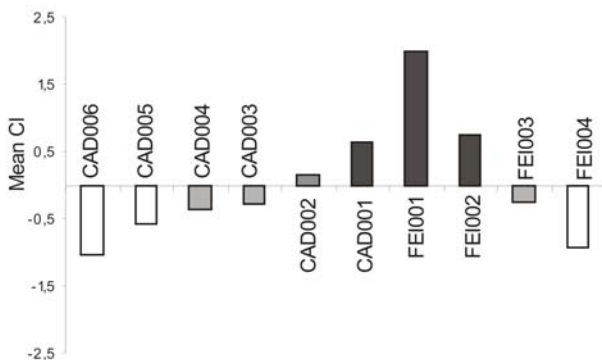

Figure 3 - Spatial variation of the mean scores in factor 1, arbitrated as water contamination indexes (*CI*). Positive values indicate sites with poorer environmental quality.

Concerning the possibility of conversion of Cr (III) to the hexavalent toxic form, the dissolved

oxygen alone would not cause a measurable oxidation, but the presence of MnO_2 could catalyze the reaction (ATSDR, 1999). Schröder & Lee (1975) suggest that a potential oxidation of Cr (III) in the presence of MnO_2 demands the sorption of the cation to given sites, which, in general, are scarce as compared to the total surface area. If, by chance, Cr (VI) were to occur in the environmental conditions studied, a reduction to Cr(III) would be probably favored, due to the complexation of Cr with natural or anthropogenic organic materials (Armienta *et al*. 2001).

Until the finished leather is obtained, many toxic substances may be introduced into the surrounding environment. Even if small, the increased content of metals such as Cu (total and dissolved) and dissolved Ni observed in the waters that are more affected by tanneries could be considered as caused by impurities in the products used in tanning. Cu could also be associated with the use of dyes and paints in the leather finish. The contents of these metals are however, close to baseline and to the detection limit of the analytic method, and so far have not arise great concern in the area investigated.

The relatively high content of alkaline and alkaline earth metals in the tannery concentration area is probably due to the use of several salts and bases, both in the production processes and in the effluent treating (sodium and calcium formiate, sodium bicarbonate, sodium carbonate, borax, sodium sulfide, sodium bisulfite, sodium chloride, sodium hydroxide, calcium hydroxide, potassium hydroxide, potassium alum, magnesium oxide, among others). One of the main characteristics of tannery wastewaters is the increased hardness, represented by high Ca and Mg contents (Schünemann *et al*. 1983).

As to temporal variability of water quality, figure 4 relates the mean values of the contamination indexes to the mean values of stream flows obtained at the different collection dates (Table 8). Considering the variables highlighted in the first factor, a lower water quality was found in January 2000, when the lowest flows occurred. This sampling revealed low water availability conditions, with the occurrence of a flow equal to 2.2 m^3/s at collection point CAD001. The flow permanence curve showed a probability of only 8% for the local occurrence of river discharges equal to or below this value over time. According to a procedure described by Lanna (2001), the permanence curve was built with daily flow measures data at the Costa do Cadeia station

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(code 87250000 of the National Water Agency), referring to the 1970-1995 period.

Figure 5 presents the spatial variation of the second factor scores. Increased scores were observed in October 1999, during the period of high water availability. On that date, at point CAD001, a 48,5 m^3/s flow was recorded (Table 8), with a chance less than 20% of being surpassed or equalled over time. Figure 6 shows the variation of second factor scores and stream flow in the same date, which was the only one that presented similar tendencies for both variables throughout the length of Cadeia and Feitoria rivers. The pattern observed during a period with greater water availability revealed the influence of high flows on the occurrence of suspended materials, naturally rich in Fe and Al, in the water. Besides erosion and silting processes, this behavior is probably associated with the resuspension of materials from the riverbed itself. The response of the scores to the high river discharge event was more marked in Feitoria river where finer-grained materials are deposited. Due to the greater stream competency, conditions in Cadeia river usually appear to be more favorable for exporting fine materials to the mouth or even to Caí river.

Table 8 - Flows and drainage areas of the sub-basins of the Cadeia and Feitoria rivers.

Local	Dramage area (km²)	Σ area (km²)	Stream flow (m³/s)			
			Jul 99	Oct 99	Jan 00	Apr 00
FEI004	74.6	74.6	0.70	3.29	0.30	0.99
FEI003	62.1	136.8	1.29	6.03	0.55	1.81
FEI002	61.6	198.3	1.87	8.75	0.80	2.63
FEI001	16.2	214.6	2.02	9.47	0.86	2.84
CAD006	67.4	67.4	0.52	3.88	0.15	1.05
CAD005	213.5	280.8	2.16	16.2	0.61	4.40
CAD004	130.1	410.9	3.16	23.6	0.89	6.43
CAD003	60.0	470.9	3.63	27.1	1.01	7.37
CAD002	55.7	526.6	4.06	30.3	1.13	8.24
CAD001	147.6	888.7	6.73	48.5	2.23	9.53
Mouth	8.0	(*)				
Total	896.8	888.7				

*Area not considered (it lies downstream from site CAD001)

Figure 4 - Temporal variation of the mean of water contamination indexes and corresponding stream flows (positive values of the indexes indicate sampling dates when a lower water quality was found).
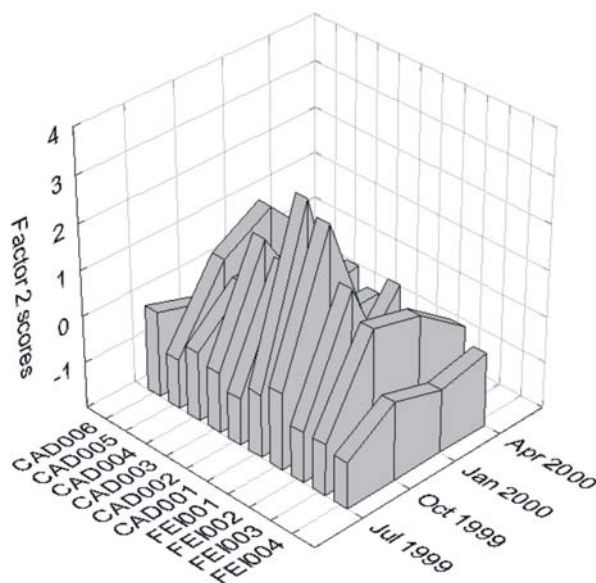
Figure 5 - Spatial and temporal variation of the scores obtained in the second component of factorial analysis (natural contribution).

Randomization tests

Obtaining $P=0.0001$, both when comparing dates and sites, indicated that at least a pair of dates and a pair of sites were significantly different, and that the contrasts should be analyzed individually. Considering the set of variables evaluated and a 5% level of significance, all collection dates were dissimilar from each other (Table 9). This result highlighted the great variation in water quality over time, and the instantaneous character of physicochemical measurements, when dealing with this environmental compartment. For $\alpha=0.05$, the comparison of sampling sites indicated a dissimilarity between the controls and points FEI002, FEI001 and CAD001 that suffered the greatest impact of tannery activity (Table 10). If a greater chance of error were considered in the statistical analysis ($\alpha=0.10$), point CAD002 would also be significantly different from the respective control (CAD006), since it showed indications of environmental degradation, possibly due to the influence of tannery activities in the municipality of São José do Hortêncio. The results of the randomization tests ratified those obtained

using factorial analysis showing the same sites as relatively more contaminated. In the two rivers, the points located between the controls and the contaminated region of the lower reach alternately presented significant similarities or differences with points located upstream (less contamination) or downstream (more contamination), which configured its intermediary position in the hierarchy of environmental water quality.

Table 9 - Result of randomization tests comparing the sampling dates.

Contrasts	Dates	P	Ho (α=0.05)
1 -1 0 0	Jul 99-Oct 99	0.0001	Rejected
1 0 -1 0	Jul 99-Jan 00	0.0005	Rejected
1 0 0 -1	Jul 99-Apr 00	0.0064	Rejected
0 1 -1 0	Oct 99-Jan 00	0.0001	Rejected
0 1 0 -1	Oct 99-Apr 00	0.0012	Rejected
0 0 1 -1	Jan 00-Apr 00	0.0003	Rejected

Spatial representation of the results

Tables 11 and 12 contain, respectively, the values of the quartiles used in categorizing the first

factor scores, and the results of the classification of sites. The final product of the study is presented in figure 7, where these sites were marked on a map, according to the relative degree of water quality. As to the variables analyzed, the control points (CAD006 and FEI004) and site CAD005 (Joaneta) were outstanding for their better environmental quality. In the two rivers, the water quality was degraded from the sources to the mouth, with greater con-
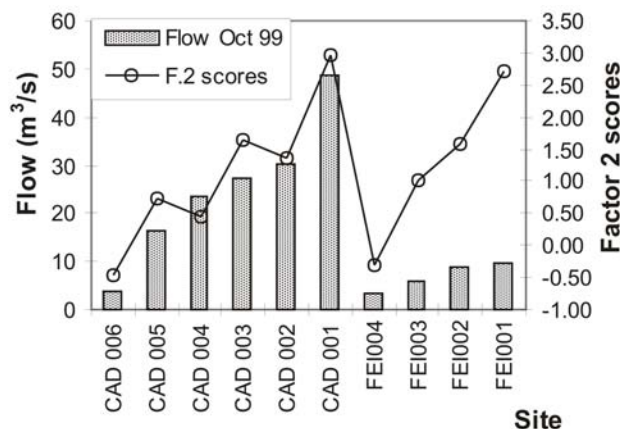

Figure 6 - Variation of flows and scores obtained in the second component of factorial analysis, in October 1999 (natural contribution).
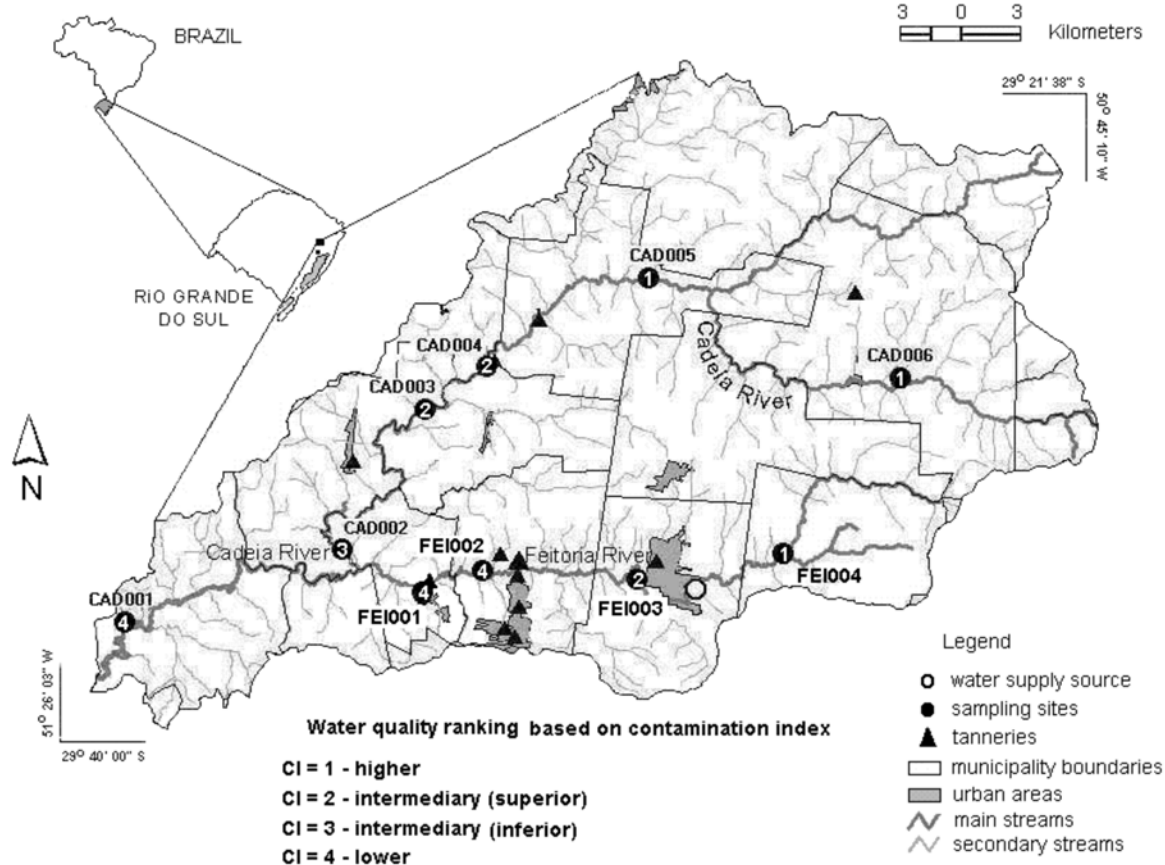

Figure 7 - Location of the study area and classification of sampling sites regarding water quality in the period from July 1999 to April 2000.

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Table 10 - Result of randomization tests comparing the sampling sites.

Contrasts	Locals	P	Comparison to alpha	Ho
1 -1 0 0 0 0 0 0 0	FEI004 - FEI003	0.3562	> 0.05	Accepted
1 0 -1 0 0 0 0 0 0	FEI004 - FEI002	0.0269	< 0.05	Rejected
1 0 0 -1 0 0 0 0 0	FEI004 - FEI001	0.0001	< 0.05	Rejected
1 0 0 0 -1 0 0 0 0	FEI004 - CAD006	0.9407	> 0.05	Accepted
1 0 0 0 0 -1 0 0 0	FEI004 - CAD005	0.4674	> 0.05	Accepted
1 0 0 0 0 0 -1 0 0	FEI004 - CAD004	0.3834	> 0.05	Accepted
1 0 0 0 0 0 0 -1 0	FEI004 - CAD003	0.2834	> 0.05	Accepted
1 0 0 0 0 0 0 0 -1 0	FEI004 - CAD002	0.1393	> 0.05	Accepted
1 0 0 0 0 0 0 0 0 -1	FEI004 - CAD001	0.0232	< 0.05	Rejected
0 1 -1 0 0 0 0 0 0	FEI003 - FEI002	0.2015	> 0.05	Accepted
0 1 0 -1 0 0 0 0 0	FEI003 - FEI001	0.0022	< 0.05	Rejected
0 1 0 0 -1 0 0 0 0	FEI003 - CAD006	0.2298	> 0.05	Accepted
0 1 0 0 0 -1 0 0 0	FEI003 - CAD005	0.5441	> 0.05	Accepted
0 1 0 0 0 0 -1 0 0	FEI003 - CAD004	0.8319	> 0.05	Accepted
0 1 0 0 0 0 0 -1 0 0	FEI003 - CAD003	0.7315	> 0.05	Accepted
0 1 0 0 0 0 0 0 -1 0	FEI003 - CAD002	0.7927	> 0.05	Accepted
0 1 0 0 0 0 0 0 0 -1	FEI003 - CAD001	0.3027	> 0.05	Accepted
0 0 1 -1 0 0 0 0 0	FEI002 - FEI001	0.0862	> 0.05	Accepted
0 0 1 0 -1 0 0 0 0	FEI002 - CAD006	0.0127	< 0.05	Rejected
0 0 1 0 0 -1 0 0 0	FEI002 - CAD005	0.0470	< 0.05	Rejected
0 0 1 0 0 0 -1 0 0	FEI002 - CAD004	0.1186	> 0.05	Accepted
0 0 1 0 0 0 0 -1 0 0	FEI002 - CAD003	0.1318	> 0.05	Accepted
0 0 1 0 0 0 0 0 -1 0	FEI002 - CAD002	0.4702	> 0.05	Accepted
0 0 1 0 0 0 0 0 0 -1	FEI002 - CAD001	0.6937	> 0.05	Accepted
0 0 0 1 -1 0 0 0 0	FEI001 - CAD006	0.0001	< 0.05	Rejected
0 0 0 1 0 -1 0 0 0	FEI001 - CAD005	0.0002	< 0.05	Rejected
0 0 0 1 0 0 -1 0 0	FEI001 - CAD004	0.0008	< 0.05	Rejected
0 0 0 1 0 0 0 -1 0 0	FEI001 - CAD003	0.0010	< 0.05	Rejected
0 0 0 1 0 0 0 0 -1 0	FEI001 - CAD002	0.0104	< 0.05	Rejected
0 0 0 1 0 0 0 0 0 -1	FEI001 - CAD001	0.0493	< 0.05	Rejected
0 0 0 0 1 -1 0 0 0	CAD006 - CAD005	0.4309	> 0.05	Accepted
0 0 0 0 1 0 -1 0 0 0	CAD006 - CAD004	0.2748	> 0.05	Accepted
0 0 0 0 1 0 0 -1 0 0	CAD006 - CAD003	0.1657	> 0.05	Accepted
0 0 0 0 1 0 0 0 -1 0	CAD006 - CAD002	0.0693	> 0.05	Accepted
0 0 0 0 1 0 0 0 0 -1	CAD006 - CAD001	0.0121	< 0.05	Rejected
0 0 0 0 0 1 -1 0 0 0	CAD005 - CAD004	0.7958	> 0.05	Accepted
0 0 0 0 0 1 0 -1 0 0	CAD005 - CAD003	0.6732	> 0.05	Accepted
0 0 0 0 0 1 0 0 -1 0	CAD005 - CAD002	0.2710	> 0.05	Accepted
0 0 0 0 0 1 0 0 0 -1	CAD005 - CAD001	0.0676	> 0.05	Accepted
0 0 0 0 0 0 1 -1 0 0	CAD004 - CAD003	0.9952	> 0.05	Accepted
0 0 0 0 0 0 1 0 -1 0	CAD004 - CAD002	0.6412	> 0.05	Accepted
0 0 0 0 0 0 1 0 0 -1	CAD004 - CAD001	0.1774	> 0.05	Accepted
0 0 0 0 0 0 0 1 -1 0	CAD003 - CAD002	0.7041	> 0.05	Accepted
0 0 0 0 0 0 0 1 0 -1	CAD003 - CAD001	0.1956	> 0.05	Accepted
0 0 0 0 0 0 0 0 1 -1	CAD002 - CAD001	0.6002	> 0.05	Accepted

Table 11 - Values of the quartiles used in categorizing the scores in factor 1.

Lower quartile	Median	Upper quartile
-0.612	-0.234	0.472

Table 12 - Result of the categorization of first factor scores (or water contamination indexes).

Number of points	Site	Classification	Symbol
4 to 7	CAD006, FEI004, CAD005	Higher quality	❶
8 to 10	CAD004, CAD003, FEI003	Higher intermediary quality	❷
11 to 13	CAD002	Lower intermediary quality	❸
14 to 16	CAD001, FEI002, FEI001	Lower quality	❹

tamination of sites FEI002 (Ivoti),FEI001 (Lindolfo Collor) and of the region of Cadeia river mouth (point CAD001 at São Sebastião do Caí). The environmental misadjustment found in the lower reach of Feitoria river showed a close relationship with the concentration of tanneries in this area, the lower slope of the terrain and the comparatively low dilution capacity of the water in this part of the basin.

CONCLUSIONS

Save for a few exceptions, the concentration of metals evaluated in Cadeia and Feitoria rivers was in agreement with the Brazilian water quality standards. Although surpassing the respective limits, the increased dissolved aluminum and iron contents probably reflected the conditions of the natural environment. However, it was observed that the water quality diminished from headwaters up to mouth along both streams, and increased levels of contaminants that are typical of tannery inputs were found at the lower reach of the watershed. The water contamination also showed association to flow variations, and a poorer quality was observed in January, during the dry period.

The application of multivariate statistics to the database helped to pinpoint the relevant variables to describe the environmental scenario, and helped to identify tendencies over time and space. Although the conclusions cannot be generalized and are specific to the data evaluated, obtaining a water contamination index not only highlighted the relative environmental quality between collection points, it also delimited the area which is most influenced by the tannery plants. The spatial visualization of the results allowed the evaluation of the extent of environmental contamination in the study area, and it may be very useful in decision-making concerning priority actions to recover degraded areas in the state of Rio Grande do Sul.

REFERENCES

ABNT – Associação Brasileira de Normas Técnicas. 1987. **Água – Preservação e técnicas de amostragem de efluentes líquidos e corpos receptores (NBR9898)**. Rio de Janeiro, ABNT.

APHA - American Public Health Association. 1992. **Standard Methods for the Examination of Water and Wastewater**. Washington DC, APHA. 18th ed.

APHA - American Public Health Association. 1995. **Standard Methods for the Examination of Water and Wastewater**. Washington DC, APHA. 19th ed.

Armienta, M.A.; Rodríguez, R.; Ceniceros, N.; Juárez, F. & Cruz, O. 1996. Distribution, origin and fate of chromium in soils in Guanajuato, Mexico. **Environmental Pollution**, **91**(3):391-397.

Armienta, M.A.; Morton, O.; Rodríguez, R.; Cruz, O. & Aguayo, N. 2001. Chromium in a tannery wastewater irrigated area, León Valley, Mexico. **Bulletim of Environmental Contamination and Toxicology**, **66**:189-195.

Aravindham, R.; Madham, B.; Rao, J.R.; Nair, B.U. & Ramasami, T. 2004. Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. **Environmental Science Technology**, **38**:300-306.

ATSDR - Agency for Toxic Substances and Disease Registry. 1999. **Toxicological profile for chromium**. Disponível em: http://www.atsdr.cdc.gov/toxprofiles/tp7.html. Acesso em: nov. 2004.

Baisch, P. 1994. **Les oligo-elements metalliques du systeme fluvio-lagunaire dos Patos. (Bresil)** : flux et devenir. Bordeaux. 358p. Tese de Doutorado em Geologia Marinha, L'Université de Bordeaux I.

Berner, E.K.; Berner, R.A. 1987. **The global water cycle**. Englewood Cliffs, Prentice-Hall Inc., 397p.

Bowen, H.J.M. 1979. **Environmental chemistry of the elements**. London, Academic Press, 333p.

Brownlow, A.J. 1972. **Geochemistry**. New Jersey, Prentice-Hall, 498p.

Buerge, I.J. & Hug, S.J. 1997. Influence of mineral surfaces on Chromium(VI) reduction by Iron(II). **Environmental Science Technology**, **33**:4285-4291.

Campos, S.H. 2006. **A indústria de couros no Brasil:** desempenho superior ao da indústria calçadista em 2006. Disponível em: http://www.fee.tche.br/sitefee/download/indicadores/34_02/6_parte.pdf. Acesso em: out. 2006.

Carré, M.C.; Vulliermet, A.; Vulliermet, B. 1994. **Tannerie et environnement**. Lion, Centre Technique du Cuir, 412p.

CETESB - Companhia de Tecnologia de Saneamento Ambiental. 1977. **Guia técnico de coleta de amostras de água**. São Paulo, CETESB, 257p.

CONAMA - Conselho Nacional do Meio Ambiente. Resolução nº 357 de 17 de março de 2005. **Diário Oficial da União**, Brasília, 18 de março de 2005, p.59-60.

Fachel, J.M.G. 1976. **Análise fatorial**. São Paulo. 81p. Dissertação de Mestrado em Estatística, Instituto de Matemática e Estatística, Universidade de São Paulo.

FEPAM/FINEP, Vargas, V.M.F. (coord.). 2003. **Estratégias ecotoxicológicas de avaliação de risco**. Porto Alegre, FEPAM, Relatório de Projeto PADCT/CIAMB.

Florence, T.M. 1982. The speciation of trace elements in waters. **Talanta**, **29**:345-364.

Förstner, U.; Wittman, G.T.W. 1981. **Metal pollution in the aquatic environment**. Berlin, Springer-Verlag, 2nd ed., 486p.

Guterres, M. 1997. Considerações sobre curtimento ao couro e meio ambiente. **Revista do Couro**, **28**:28-29.

Haase, J. & Possoli, S. 1993. Estudo da utilização da técnica de análise fatorial na elaboração de um índice de qualidade da água: comparação entre dois regimes hidrológicos diferentes, RS **Acta Limnologica Brasiliensis**, **6**:245-255.

Hart, B.T. & Hines, T. 1995. Trace elements in rivers. In: Salbu, B. & Steinnes, E. (eds). **Trace elements in natural waters**. Boca Raton, CRC Press. p.203-221.

Hatje, V. 1996. **Caracterização por metais pesados no rio dos Sinos – RS:** uma abordagem dinâmica a partir de balanços de massa. Niterói. 101p. Dissertação de Mestrado em Geoquímica Ambiental, Instituto de Geociências, Universidade Federal Fluminense.

Jackson, D.A. 1993. Stopping rules in principal component analysis: a comparison of heuristical and statistical approaches. **Ecology**, **74**:2204-2214.

Jordão, C.P.; Pereira, J.L. & Jham, G.N. 1997. Chromium contamination in sediment, vegetation and fish caused by tanneries in the State of Minas Gerais, Brazil. **Science of the Total Environment**, **207**:1-11.

Kim, J.G.; Dixon, J.B.; Chuseuei, C.C. & Deng, Y. 2002. Oxidation of Chromium(III) to (VI) by manganese oxides. **Soil Science Society of America Journal**, **66**:306-315.

Krieger, E.I.F. 2000. **Avaliação da contaminação de águas subterrâneas na área de influência da Usina de Tratamento de**

Resíduos S/A – UTRESA, em Estância Velha (RS). Porto Alegre. 142p. Dissertação de Mestrado em Ecologia, Instituto de Biociências, Universidade Federal do Rio Grande do Sul.

Lanna, A.E. 2001. Elementos de estatística e probabilidades. In: Tucci, E.M. (organizador). **Hidrologia – Ciência e Aplicação**, 2ª ed.. Porto Alegre, Editora da Universidade/UFRGS. p.79-176.

Laybauer, L. 1995. **Análise das transferências de metais pesados em águas e sedimentos fluviais na região das minas de Camaquã, RS**. Porto Alegre. 164p. Dissertação de Mestrado em Geociências, Instituto de Geociências, Universidade Federal do Rio Grande do Sul.

Marsh, T.L. & McInerney, M.J. 2001. Relationship of hydrogen bioavailability to chromate reduction in aquifer sediments. **Applied and Environmental Microbiology**, **67**(4):1517-1521.

Nakayasu, K.; Fukushima, M.; Sasaki, K.; Tanaka, S. & Nakamura, H. 1999. Comparative studies of the reduction behaviour of chromium(VI) by humic substances and their precursors. **Environmental Toxicology and Chemistry**, **18**(6):1085-1090.

Nriagu, J.O. 1988. A silent epidemic of environmental poisoning. **Environmental Pollution**, **50**:139-161.

Pillar, V.D.P. 2000. **MULTIV - Software para análise multivariada e testes de aleatorização**. Porto Alegre, UFRGS.

Pillar, V.D.P. & Orlóci, L. 1996. On randomization testing in phytoecoenology: multifactor comparisons of relevé groups. **Journal of Vegetation Science**, **7**:585-592.

Rodrigues, M.L.K.; Pillar, V.D.P.; Raya-Rodríguez, M.T. & Filho, S.P. 2003. Aplicação de ordenação bootstrap na identificação de padrões de distribuição de metais em sedimentos da Bacia Hidrográfica do Rio Caí (RS, Brasil). **Brazilian Journal of Ecology**, **5-6**(1-2):39-45.

Rodrigues, M.L.K. & Raya-Rodríguez, M.T. 2003. Statistical factor analysis of heavy metal pollution in the Caí River Basin sediments (Brazil). In: SYMPOSIUM ON CONTAMINATED SEDIMENTS, 2, Québec. **Transactions …** Québec, Locat, J.; Galvez-Cloutier, R.; Chaney, R.C. & Demars, K. (eds.). p.349-399.

Rodrigues, M.L.K.; Raya-Rodríguez, M.T. & Pillar, V.D.P. 2003. Randomization tests: a statistical tool to assess heavy metal pollution in Caí River Basin sediments (RS, Brazil). In: Locat, J.; Galvez-Cloutier, R.; Chaney, R.C. & Demars, K. (eds.). **Contaminated Sediments**. West Conshohocken, ASTM International. STP 1442, p.62-72.

Schroeder, D.C. & Lee, G. F. 1975. Potential transformations of chromium in natural waters. **Water, Air, and Soil Pollution**, **4**:355-365.

Schünemann, A.M.C.; Paz, A.M.A.S.; Krieger, E.I.F. ... [*et al*.]. 1983. Reciclo dos banhos de caleiro e oxidação dos sulfetos contidos nos efluentes de curtumes. In: CONGRESSO BRASILEIRO DE ENGENHARIA SANITÁRIA E AMBIENTAL, 12, Camboriú, SC. **Resumos…** Camboriú, ABES.

Teixeira, E.C.; Fachel, J.M.G.; Vecchio, G.; Migliavacca, D.; Sanchez, J.C.D., Haase, J. & Cobalchini, S. 2000. Proposal of a water quality index for tha Baixo Jacuí region, RS, Brazil. **Geochimica Brasiliensis**, **14**(2):209-217.

Valaoras, G.; Gogliano, V.J. & Herman, G. 1991. Risk assessment methodology applications in Greece: exposure to pesticides and chromium. In: CONFERENCE ON ENVIRONMENTAL SCIENCE AND TECHNOLOGY,2, Aegean, Greece, 1991. **Proceedings…** Aegean, University of Aegean.

Vitale, R.J.; Mussoline, G.R.; Rinehimer, K.A. 1997. Environmental monitoring of chromium in air, soil, and water. **Regulatory Toxicology and Pharmacology**, **26**:80-85.

WHO - World Health Organization. 2004**. Manganese and its compounds:** environmental aspects. Disponível em: http://www.inchem.org/documents/cicads/cicads/cicad63.htm. Acesso em: set. 2005.

Wittbrodt, P.R. & Palmer, C.D. 1996. Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances. **Environmental Science and Technology**, **30**: 2470-2477.