Assessment of Soil Solution Chemicals after Tannery Effluents Disposal

[1]Célia A. Surita, [1,2]Thomas Gloaguen, [1,3]Célia R. Montes and [4]Carlos T. S. Dias

[1]Núcleo de Pesquisas em Geoquímica e Geofísica da Litosfera (Nupegel), Universidade de São Paulo.
Av. Pádua Dias, 11, 13418-900, Piracicaba, São Paulo, Brazil.

[2]Instituto de Geociências, Universidade de São Paulo. Rua do Lago, 562, 05508-900, São Paulo, Brazil.

[3]Departamento de Solos e Nutrição de Plantas, Universidade de São Paulo. Av. Pádua Dias, 11, 13418-900, Piracicaba, São Paulo, Brazil.

[4]Departamento de Ciências Exatas, Universidade de São Paulo. Av. Pádua Dias, 11, 13418-900, Piracicaba, São Paulo, Brazil

Abstract: Knowledge about soil solution chemicals is important for assessing their mobility, availability, migration to groundwater and toxicity to plants. The objective of this study was to apply factor analysis to data obtained on soil solution chemicals during a one-year monitoring program in a controlled experiment with tannery effluents disposed on the soil surface, to extract information on their relationship and identify the main contaminants. Seventeen chemical parameters were monitored at six different depths on soil profile, focusing on metals and nitrate in soil solution. Four Factors accounted for 79.20% of the total variance, of which the most important were: Factor 1 (48.35%) showed significant loadings for Mn^{2+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, Pb^{2+} and electric conductivity, strongly influenced by high load effluent disposal; Factor 2 (12.21%) was related with SO_4^{2+}, Factor 3 (10.16%) associated with Cu^{2+} and Zn^{2+} and Factor 4 (8.49%) associated with nitrogen mineralization dynamics after high disposal.

Key words: Soil solution, groundwater, tannery effluents, factor analysis

INTRODUCTION

Industrial activities are capable of generating soil and groundwater pollution as a result of the emission of liquid effluents or waste disposal practices[1-5]. The tanning industry is considered an activity with elevated potential for environmental pollution all over the world. Tanning processes use substantial amounts of chromium salts and other heavy metals, sulfide and organic compounds[6]. Brazilian bovine hide tanneries usually consume 20 to 40 m^3 of water per ton of processed hide[7]. According to IBGE[8], it is estimated that about 35 million hides from chrome processing were tanned in 2005, generating 24 to 49 million m^3 of wastewater and 0.6 to 1.2 million tons of sludge.

A great deal of these effluents has been continuously discharged in soils in the northeast region of the State of São Paulo (SE, Brazil), affecting the soil and groundwater quality, but the effects of these practices are not yet well known. These soils are mineral soils formed under tropical climates subjected to intense weathering. They have a sandy clay loam to sandy loam texture, low activity clay, mainly kaolinite and low organic matter content[9].

It is known that heavy metals added to soils are rapidly and specifically adsorbed by the solid fraction. However their availability, potential toxicity and mobility within the soil profile will depend upon the binding forms with clays, organic matter and hydrous oxides, oxides and oxyhydroxides; the interactions of their associations with time; the saturation of specific sites of adsorption; the crystallinity and morphology of absorbent surfaces; pH variation[10-13] and physicochemical characteristics[14].

Several studies have shown that the availability of Cr(III) in the soil solution is limited by the formation of hydroxides as $Cr(OH)_3$ and $Cr_2O_3(H_2O)$, at pHs between 6 and 12[15], or by co-precipitation with Fe, forming $(Cr_x,Fe_{1-x})(OH)_3$, $(Cr_x,Fe_{1-x})OOH$, $Fe_x,Cr_{2x}O_3$[16, 17]. Another mechanism controlling Cr availability is the adsorption on the surface of Fe, Mn and Al oxides and oxi-hydroxides and clay-minerals, at pH < 6[18, 19] and adsorption onto organic matter[20]. The Cr(III) oxidation seems to be mainly controlled by the

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Corresponding Author: Célia Alves Surita - Núcleo de Pesquisas em Geofísica e Geoquímica da Litosfera. Av. Pádua Dias, 11, 13418-900, Piracicaba, São Paulo, Brazil

sorption on Mn-oxides surfaces followed by the electron transfer and desorption of Cr(VI) and Mn^{2+}[21-23] and by MnO_2 amount[24]. Tzou *et al.*[25] showed that chromium oxidation by Mn-oxides was rapid at acidic conditions and kinetically slow at high pH, inhibited by organic ligands.

Conservative solutes move with soil water and in response to solute concentration gradients[26] and are influenced by soil hydraulic[27] and heterogeneity[28]. These studies require monitoring of a wide range of physical, chemical and biological data. Multivariate analysis is a mathematical tool that can be employed to study the interrelationship among wide data sets by reducing the dimensionality of the data variables[29-31].

Our interest in this work focuses on metal and nitrate levels in soil solution at different depths in an acid soil (Typic Haplustox) with tannery effluents disposal. The data obtained during a one-year monitoring program in a controlled experiment were subjected to factor analysis, to extract information on the relationship between soil solution chemicals and to identify the principal contaminants.

MATERIALS AND METHODS

The experiment took place in a $9m^2$-experimental plot, located in Monte Aprazível (NW of the State of São Paulo, Brazil, 20° 46'S, 49° 42'W), in the Aw climate zone, according to the Köppen classification. During the experiment (1996-1997) the annual average temperature was 25 ^{o}C and the annual average precipitation was 1400 mm. The driest period was observed between the months of July and August/97 (0 mm). The period with most rainfall was from November/96 to March/97 with precipitations from 118 mm to 321 mm.

In the experimental plot, 6 pressure-vacuum lysimeters with ceramic porous cups were installed at 0.5 m intervals to 3.0 m of depth to sample soil solution according to ASTM procedures[32]. The sampling was done applying a continuous suction of 20-40 to 60 kPa per period of 10 to 12 hours. Soil and soil solution samplings were first performed before the disposal of effluents, at the same depths. The effluents were applied to the soil in two amounts and periods: 700 L in March/1996 and 1,700 L in September/1996. The tannery effluents were collected during a whole working day and were analyzed for the determination of pH, electrical conductivity (EC), Cr_{total}, Mn, Fe_{total}, Al^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, S^{2-}, SO_4^{2-}, Cl^-, NH_3, NO_3^-, chemical oxygen demand (COD), biological oxygen demand (BOD), settleable solids (SetS) and suspended solids (SS) (Table 1). Metals

were determined by atomic absorption spectrometer, anions by spectrophotometry UV/VIS, COD by acidic chromate solution, BOD by Azide Modified Winkler Method, SS by filtration, setteable solids by Imhoff cone, by Standard Methods[33].

Soil solution samples were collected in February/96, March/96 (before disposal), May/96, June/96, July/96 (after first disposal), October/96, November/96, January/97 and March/97 (after second disposal); filtered through 0.45 μm cellulose acetate and the preservation was conducted by Standard Methods[33]. From every sample, a subsample was kept at its natural pH and used for determination of anions (NO_3^-, SO_4^{2-}, Cl^- and PO_4^{3-}) by liquid chromatography. A second subsample was acidified to pH 2 with nitric acid for metal analysis (Cr_{total}, Fe_{total}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Ca^{2+} and Mg^{2+}) by atomic absorption spectrophotometer. A third subsample was acidified to pH 2 with sulphuric acid for Na^+ and K^+ analysis by flame atomic absorption spectroscopy. Analytical data was controlled by calibration done with standard solutions in the appropriate matrix and analyzed at the beginning of series and after 10 samples series. Besides the check samples, regularly repeated analyses of the same samples were done. Electric conductivity (EC) and pH measurements were performed in situ (Table 2).

The soil samples were stored at 4ºC, dried at 25ºC, homogenized, quartered and sieved at 2 mm. They were analyzed for the determination of pH (electrode, $0.01molL^{-1}$ $CaCl_2$), organic matter, exchangeable ions and cation exchange capacity (cation exchange resin, 1N $NaHCO_3$, pH 8.5)[34], texture[35] and chemical composition (X-ray fluorescence) (Table 3).

Statistical analysis: The correlation coefficients were calculated for the 17 variables values that presented more than 6 valid cases, accepted to factor analysis. Factor analysis was performed from the correlation matrix to extract principal factors with eigenvalues greater than 1 and detect the relationship between the variables. The selected factors were subjected to normalized varimax rotation in order to define a clear pattern of loadings[36]. Analysis of variance was employed on the factor scores to evaluate the effects of effluent load and different depths on the extracted factors. The statistical analyses were carried out in Statistica software package[37].

RESULTS AND DISCUSSION

The effluents discharged into the soil presented high variability of the chemical and physical characteristics due to different quantities of processed

Table 1: Physical and chemical characteristics of effluents disposed into the soil

Effluents parameters	March-96 700L	September -96 1,700L
pH	7.1	7.5
EC (dS m^{-1})	11.5	10.9
Cr$_{total}$ (mg L^{-1})	138	41
Fe$_{total}$ (mg L^{-1})	4.4	2.2
Mn^{2+} (mg L^{-1})	0.01	0.01
Al^{3+} (mg L^{-1})	11.5	25.5
Ni^{2+} (mg L^{-1})	1.1	0.4
Cu^{2+} (mg L^{-1})	0.35	0.05
Zn^{2+} (mg L^{-1})	1.7	0.6
Pb^{2+} (mg L^{-1})	0.02	0.1
Na$^+$ (mg L^{-1})	27,400	5,800
K$^+$ (mg L^{-1})	44	23
Ca^{2+} (mg L^{-1})	355	453
Mg^{2+} (mg L^{-1})	25	15
S^{2-} (mg L^{-1})	19	26
SO$_4^{2-}$ (mg L^{-1})	4,661	576
Cl$^-$ (mg L^{-1})	14,670	3,548
NH$_3$ (mg L^{-1})	ND	1058
NO$_3^-$ (mg L^{-1})	36.0	1.2
COD (mg L^{-1})	4,081	3,232
BOD (mg L^{-1})	957	1,395
Suspended solid (mgL^{-1})	4,420	780
Settable Solids (mgL^{-1})	66	ND
Sodium adsorption ratio (mmol$_c$L^{-1})$^{-0,5}$	379	73

EC: Electrical conductivity, ND: not determined, COD: chemical oxygen demand, BOD: biological oxygen demand

hides and different batches at different days. Higher concentration of Na$^+$(5,800-27,400 mgL^{-1}) was observed comparing to Ca^{2+} (350-450 mgL^{-1}), K$^+$(23-44 mgL^{-1}) and Mg^{2+}(15-25 mL^{-1}) (Table 1). This reflects the use of large amounts of NaCl in the hide preservation stage and Na$_2$S, NaOH and Na$_2$SO$_3$ used during the tanning process. Among the heavy metals, Cr$_{total}$ was found in high concentration (41-138 mgL^{-1}) and low levels of Fe$_{total}$ (2.2-4.4 mgL^{-1}), Mn^{2+}(0.01 mgL^{-1}), Ni^{2+}(0.4-1.1 mgL^{-1}), Zn^{2+} (0.6-1.7 mgL^{-1}) and Pb^{2+}(0.10-0.02 mgL^{-1}). The Cr concentrations are much higher than the Brazilian standard for Cr bearing discharges in water bodies. The Al^{3+} presents levels between 11.5-25.5 mgL^{-1}, due to the aluminum salts used before chromium tanning. The effluents present a neutral pH value due to NaOH, Ca(OH)$_2$, Mg(OH)$_2$, CaO, used during the initial stages of tanning.

The presence of Fe$_{total}$, Mn^{2+}, Zn^{2+}, Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ in soil solution (Table 2), before effluent disposal, has been attributed to compositions of the total soil water, collected from different pore sizes, which have different mobilities[38]. The pH values of the soil solution (mean: 7.03) can reflect non equilibrium condition between soil and soil solution chemistry due to abundant rainfall (summer) that change the moisture content regulating the availability of the elements. Also, the sampling

procedures of the soil solution, duration and degree of sampler vacuum, may change pH values[39].

After the first disposal (700L), the pH decreased in the subsurface (0.5 m) attributed to nitrogen transformations, which affect the acid-base chemistry of the soil and the soil solution. These conditions increased the solubility of Al^{3+} and Mn^{2+}. Chromium was not observed in soil solution, probably due to the occurrence of reducing agents, such as ferrous iron and organic matter and sorption onto iron oxi-hydroxides that might contribute to the retention of chromium in trivalent state.

With the second disposal, it was observed that ion concentration increased up to approximately 2.0 m in depth indicating movement of Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, NO$_3^-$ and Mn^{2+}. In spite of the great amount disposed (1,700 L), the concentration of Cr$_{total}$ was below the detection limit of the analytical method. In some samples, iron concentration was below the detection limit, indicating that it may have contributed to retention of chromium in the trivalent state probably through co-precipitation reactions, reducing the chance of toxicity for plants and downward migration in the soil profile.

The correlation coefficient matrix is shown in Table 4. The highest correlation (r=0.93; p<0.01) occurred between Ca^{2+} and Mg^{2+} and Mn^{2+} versus Ca^{2+} and Mg^{2+} (r=0.85, p<0.01). Strong and negative correlations were obtained for pH versus Mn^{2+} (r>-0.77, p<0.01). The Mn^{2+} presented low concentrations in effluents, but the increase of its availability in soil solution (Table 2), might be related to Mn-oxide reduction caused by Cr(III) and pH decrease. The availability of Al^{3+} was attributed to pH decrease (pH<5.0), according to McBride[40] and to higher potential acidity of these acid soil[41]. Pb^{2+} also present a significant but lower correlation with pH(-0.48), pointing to heavy metal mobilization and acidification processes. The positive correlation of NO$_3^-$ with Ca^{2+}, Mg^{2+}, Mn^{2+} and Cl$^-$ (r>0.40 p<0.01) can be the result of a similar solubility and mobility through the unsaturated zone.

R-mode factor analysis: Eigenvalues indicated that the first four Factors accounted for 79.20% of the total variance, where all these eigenvalues are greater than one (Table 5). The first Factor accounted for 48.35% of the total variance and presented high loadings (>0.7) for EC, Mn^{2+}, Pb^{2+}, Na$^+$, K$^+$, Ca^{2+}, Mg^{2+} and Cl$^-$. This Factor, called "salinity", emphasizes the important role of Na$^+$, Mg^{2+}, K$^+$, Ca^{2+}, Cl$^-$, Mn^{2+} and Pb^{2+} in the composition of soil solution, related to the effect of high load effluent disposal, with high salinity.

Table 2:   Soil solution quality attributes at different depths before and after effluent disposal

	data	Effluent (L)	depth (m)	pH	EC dSm⁻¹	Cr$_{total}$	Fe$_{total}$	Mn²⁺	Al³⁺	Zn²⁺	Cu²⁺	Ni²⁺	Pb²⁺	Na⁺	K⁺	Ca²⁺	Mg²⁺	NO₃⁻	SO₄²⁻	Cl⁻
													mgL⁻¹							
before disposal	fev96	0	0.5	8.1	0.23	BDL	0.06	BDL	BDL	0.83	0.18	BDL	BDL	11.3	22.5	8.10	3.85	3.8	17	7.0
	fev96	0	1.0	7.6	0.16	BDL	0.06	BDL	BDL	0.59	BDL	BDL	BDL	7.0	20.0	5.15	2.65	n.a	5	4.7
	fev96	0	1.5	7.7	0.29	BDL	n.a	0.02	BDL	0.17	0.09	BDL	BDL	9.0	34.0	9.70	5.05	75.5	2	11.3
	fev96	0	2.0	6.9	0.31	BDL	0.10	0.04	BDL	0.66	0.27	BDL	BDL	10.0	12.0	16.15	8.35	85.7	4	20.5
	fev96	0	2.5	6.7	0.23	BDL	0.15	0.02	BDL	1.24	2.14	BDL	BDL	11.5	12.0	11.25	6.50	49.4	4	6.4
	fev96	0	3.0	6.6	0.20	BDL	0.07	0.04	BDL	1.11	2.62	BDL	BDL	3.8	8.8	7.65	5.00	29.2	7	4.1
	mar96	0	0.5	7.2	0.21	BDL	0.09	0.00	BDL	0.10	BDL	BDL	BDL	11.3	22.5	7.75	3.95	2.0	18	9.0
	mar96	0	1.0	7.1	0.14	BDL	0.05	0.02	BDL	0.21	BDL	BDL	BDL	7.0	20.0	7.90	3.85	4.0	2	7.0
	mar96	0	1.5	6.8	0.27	BDL	0.07	0.03	BDL	0.32	BDL	BDL	0.11	9.0	34.0	13.05	6.25	93.0	1	11.0
	mar96	0	2.0	6.5	0.39	BDL	0.16	0.04	BDL	0.22	BDL	BDL	0.08	10.0	12.0	26.00	12.00	145.0	2	6.0
	mar96	0	2.5	6.6	0.21	BDL	0.05	0.03	BDL	0.21	BDL	BDL	BDL	11.5	12.0	11.30	6.05	57.0	2	4.0
	mar96	0	3.0	6.6	0.17	BDL	0.07	0.02	BDL	0.11	BDL	BDL	0.17	3.8	8.8	10.25	7.95	51.0	3	4.0
after first disposal	may96	700	0.5	6.4	1.99	BDL	0.10	2.67	BDL	0.53	BDL	0.14	0.14	1380.4	102.5	170.00	49.00	528.0	98	70.0
	may96	700	1.0	7.4	0.12	BDL	0.15	BDL	BDL	0.14	BDL	BDL	0.09	3.9	10.2	7.55	2.65	28.6	BDL	6.0
	may96	700	1.5	7.0	0.26	BDL	0.37	BDL	BDL	0.07	BDL	BDL	0.07	6.1	24.1	10.85	5.00	114.4	BDL	8.5
	may96	700	2.0	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
	may96	700	2.5	6.6	0.20	BDL	0.21	0.02	BDL	0.11	BDL	BDL	0.09	10.4	11.9	9.40	6.55	88.0	n.a	4.5
	may96	700	3.0	6.9	0.19	n.a	n.a	n.a	n.a	n.a	n.a	BDL	n.a	n.a	n.a	n.a	n.a	85.8	0	4.5
	jun96	700	0.5	5.5	3.65	BDL	0.24	1.40	0.80	0.97	BDL	BDL	0.06	676.1	33.8	43.00	13.50	327.8	713	410.0
	jun96	700	1.0	7.3	0.12	BDL	0.17	BDL	BDL	0.19	BDL	BDL	0.17	7.5	13.8	11.40	3.60	41.8	5	7.5
	jun96	700	1.5	8.0	0.27	BDL	0.08	BDL	BDL	0.18	BDL	BDL	0.06	10.0	37.5	11.00	4.80	103.4	5	11.0
	jun96	700	2.0	7.1	0.45	BDL	0.16	0.08	BDL	0.67	BDL	BDL	0.07	13.8	43.8	37.90	14.70	202.4	5	20.0
	jun96	700	2.5	6.3	0.19	BDL	0.21	0.10	BDL	0.16	BDL	BDL	0.08	16.3	12.5	16.10	9.00	85.8	5	20.0
	jun96	700	3.0	6.7	0.21	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	28.0
	july96	700	0.5	4.1	1.99	BDL	0.32	1.91	6.90	1.51	BDL	0.04	0.23	n.a	n.a	50.40	13.20	127.6	n.a	n.a
	july96	700	1.0	7.1	0.10	BDL	0.36	BDL	BDL	0.19	BDL	BDL	0.11	8.0	17.5	5.30	1.80	187.0	BDL	17.5
	july96	700	1.5	6.8	0.25	BDL	0.06	BDL	BDL	0.05	BDL	BDL	BDL	5.7	34.5	11.30	4.60	90.2	1	14.5
	july96	700	2.0	6.7	0.43	BDL	0.11	0.06	BDL	0.19	BDL	BDL	BDL	4.1	39.5	32.00	13.20	204.6	BDL	22.5
	july96	700	2.5	6.3	0.17	BDL	0.28	0.02	BDL	0.15	BDL	BDL	BDL	7.6	9.1	6.10	5.30	61.6	1	12.5
	july96	700	3.0	6.2	0.24	0.05	0.12	0.04	BDL	0.41	BDL	BDL	BDL	5.5	9.9	17.20	9.80	75.5	BDL	11.0
after second disposal	oct96	1700	0.5	7.1	0.63	0.06	0.26	0.66	BDL	1.57	BDL	0.07	0.10	1010.0	10.0	85.50	16.60	1782.0	762	584.2
	oct96	1700	1.0	6.1	1.18	BDL	0.24	3.93	1.80	0.64	BDL	0.10	0.17	1090.0	390.0	218.00	112.50	38.7	2116	2745.3
	oct96	1700	1.5	5.4	1.06	BDL	0.12	4.70	BDL	0.55	0.03	0.09	0.34	1640.0	190.0	150.00	85.50	44.0	13	3565.7
	oct96	1700	2.0	6.0	0.43	BDL	0.09	1.80	n.a	0.56	BDL	0.08	0.15	600.0	70.0	161.50	49.00	671.0	2	889.4
	oct96	1700	2.5	6.1	0.36	BDL	0.15	0.06	BDL	0.36	BDL	BDL	0.06	24.0	14.5	14.35	12.60	165.0	2	19.2
	oct96	1700	3.0	6.7	0.25	BDL	0.06	0.04	BDL	0.67	BDL	BDL	0.17	8.4	4.2	14.35	9.95	68.2	3	7.1
	nov96	1700	0.5	4.9	2.77	0.14	0.41	0.78	1.54	0.55	BDL	0.04	0.06	335.0	6.7	63.00	8.50	396.0	50	50.0
	nov96	1700	1.0	5.9	7.55	BDL	0.07	1.50	BDL	0.28	BDL	0.05	0.08	1420.0	60.0	92.00	34.75	2346.7	1050	300.0
	nov96	1700	1.5	4.7	11.16	BDL	0.09	5.70	3.95	0.14	0.03	0.09	0.18	1940.0	100.0	130.00	77.50	220.0	BDL	1500.0
	nov96	1700	2.0	4.9	6.85	BDL	BDL	1.40	2.15	0.48	BDL	0.07	0.16	2000.0	180.0	126.50	47.80	1122.0	BDL	983.3
	nov96	1700	2.5	5.7	0.54	BDL	BDL	0.02	BDL	0.22	BDL	BDL	BDL	55.0	15.0	9.80	12.15	187.0	BDL	375.0
	nov96	1700	3.0	6.0	0.25	BDL	0.05	0.03	BDL	0.49	0.03	BDL	0.30	9.0	11.0	11.40	11.90	88.0	20	5.0
	jan97	1700	0.5	6.3	0.16	BDL	BDL	0.02	BDL	0.09	BDL	BDL	BDL	10.0	0.9	4.12	0.44	5.5	8	1.4
	jan97	1700	1.0	6.2	1.06	BDL	BDL	0.09	BDL	0.12	BDL	BDL	BDL	179.6	17.5	8.50	3.55	50.6	55	n.a
	jan97	1700	1.5	5.4	5.48	BDL	BDL	1.80	0.58	0.18	BDL	0.04	0.18	1156.8	42.5	105.50	20.25	1424.5	205	497.0
	jan97	1700	2.0	4.7	10.17	BDL	0.07	7.46	5.50	0.44	0.04	0.11	0.33	1874.8	100.0	156.00	86.50	0.8	BDL	1830.0
	jan97	1700	2.5	5.4	8.24	BDL	BDL	2.06	0.85	0.49	BDL	0.07	0.25	1645.4	60.0	240.63	118.75	3.5	BDL	1300.0
	jan97	1700	3.0	5.3	6.04	BDL	BDL	0.03	2.30	1.04	0.03	0.12	0.33	638.3	40.0	31.63	33.13	5.3	12	800.0
	mar97	1700	0.5	6.0	0.09	BDL	BDL	0.03	BDL	0.21	BDL	BDL	BDL	9.0	6.9	4.20	1.30	60.7	BDL	0.5
	mar97	1700	1.0	6.5	0.71	BDL	0.05	0.02	BDL	0.17	BDL	BDL	BDL	99.7	10.0	5.20	2.60	82.7	263	11.5

Table 2: continued

	data	Effluent (L)	depth (m)	pH	EC dSm⁻¹	Cr_{total}	Fe_{total}	Mn^{2+}	Al^{3+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}
												mgL^{-1}							
after second disposal	mar97	1700	1.5	5.8	2.25	BDL	0.10	0.23	BDL	0.11	BDL	BDL	BDL	428.8	20.1	11.40	7.80	484.0	263	222.5
	mar97	1700	2.0	4.2	9.23	BDL	0.12	7.12	5.26	0.64	0.04	0.12	0.46	1306.2	111.1	122.50	61.00	1364.0	BDL	2090.0
	mar97	1700	2.5	6.0	3.11	BDL	0.15	0.80	BDL	0.40	BDL	0.04	0.06	448.7	20.0	15.10	13.50	499.4	BDL	445.0
	mar97	1700	3.0	5.3	5.59	BDL	BDL	1.60	0.98	0.49	BDL	0.06	0.19	817.6	30.2	50.75	102.00	609.4	BDL	1230.0

EC: electrical conductivity, BDL: below detection limit; n.a: not analysed

Table 3: Physical and chemical characteristics of reference soil

Parameters	depth(m)					
	0.5	1.0	1.5	2.0	2.5	3.0
pH	4.2	4.2	4.1	4.2	4,1	4,1
Organic matter (%)	1.0	1.0	0.7	0.7	0.7	0.7
Exchangeable ($mmol_c\ dm^{-3}$)						
K^+	7	2	2	1	1	3
Ca^{2+}	7	3	6	1	3	1
Mg^{2+}	5	3	6	4	6	12
H+Al	28	34	28	34	47	52
CEC	47	42	42	40	57	68
SB (%)	40	19	33	15	17	24
Texture (%)						
Clay	25	26	24	24	22	12
Silt	7	8	7	8	11	14
Sand	68	65	67	66	67	74
Total (%)						
Na_2O	0.009	BDL	BDL	BDL	BDL	0.025
K_2O	0.530	0.510	0.450	0.450	0.740	1.240
MgO	0.320	0.290	0.260	0.280	0.520	0.840
CaO	0.056	0.036	0.032	0.021	0.018	0.030
BaO	0.036	0.039	0.033	0.034	0.041	0.069
P_2O_5	0.064	0.058	0.050	0.053	0.069	0.081
SO_3	0.047	BDL	BDL	0.005	BDL	BDL
Cr_2O_3	0.060	0.051	0.049	0.050	0.070	0.070
MnO	0.060	0.059	0.057	0.061	0.062	0.074
ZnO	0.011	0.008	0.007	0.005	0.005	0.005
Fe_2O_3	5.85	6.05	5.65	6.05	7.05	6.75
Al_2O_3	9.70	9.80	9.10	9.50	10.90	9.90
SiO_2	79.60	79.40	80.70	79.80	76.60	77.40
TiO_2	2.80	2.90	2.76	2.88	3.05	2.66

BDL: below detection limit; CEC: cation exchange capacity (sum of K, Ca, Mg, H+Al), SB: percent base saturation ((sum of K, Ca, Mg / CEC)*100)

The analysis shows that application of tannery effluents increases Mn^{2+}, Pb^{2+} solubility and availability in soil solution.

Factor 2 accounted for 12.21% of the total variance related to SO_4^{2-}. It is likely that the availability of sulphate depends on higher concentrations in the effluents.

The third Factor with 10.16% of the total variance including Zn^{2+} and Cu^{2+}, indicating a behavior similar in the soil, not correlated to soil solution pH (Table 4), possibly due to adsorption reactions with inorganic and organic colloids[42].

Nitrate in high concentrations in soil solution is a contaminant that can leach and contribute to degrade groundwater quality. Therefore, NO_3^- was only included at Factor 4 (8.49%). Nitrification, a process that includes microbial activity, presents different dynamics than usual ionic processes and can explain this factor, representative of this delayed process.

The factor analysis using the three first Factors was suitable for explaining the variance of 12 of the 14 variables (Table 5) and it was shown to be an interesting tool to verify the results.

One concludes that high disposal caused significant alteration of soil solution and that clay content could enhance an accumulation of leached cationic species by clay surface adsorption at approximately 2.0 m depth. This depth showed the lower base saturation (Table 3), which contributes to cation exchange and enhances their accumulation.

Table 4: Correlation coefficients of the 17 physico-chemical variables of soil solution. The symbol * show statistical significance at 0.01 level

	pH	EC	Cr_{total}	Fe_{total}	Mn^{2+}	Al^{3+}	Zn^{2+}	Cu^+	Ni^{2+}	Pb^{2+}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	Cl^-
pH	1																
EC	-0.70*	1															
Cr_{total}	-0.05	0.07	1														
Fe_{total}	0.16	-0.10	0.30*	1													
Mn^{2+}	-0.77*	0.79*	0.11	0.04	1												
Al^{3+}	-0.71*	0.69*	0.05	-0.04	0.62*	1											
Zn^{2+}	-0.20	0.31*	0.22	0.10	0.41	0.34	1										
Cu^+	-0.06	0.13	-0.13	-0.09	0.09	0.16	0.37*	1									
Ni^{2+}	-0.64*	0.74*	0.13	-0.03	0.76*	0.72*	0.40*	0.17	1								
Pb^{2+}	-0.48*	0.46*	-0.08	0.06	0.53*	0.59*	0.27	0.10	0.69*	1							
Na^+	-0.69*	0.83*	0.02	-0.12	0.78*	0.63*	0.31*	0.10	0.79*	0.48*	1						
K^+	-0.29*	0.63*	-0.33*	-0.07	0.49*	0.49*	0.14	0.13	0.62*	0.44*	0.59*	1					
Ca^{2+}	-0.59*	0.78*	0.18	0.13	0.85*	0.63*	0.45*	0.07	0.79*	0.66*	0.71*	0.64*	1				
Mg^{2+}	-0.66*	0.80*	0.07	0.05	0.85*	0.62*	0.46*	0.13	0.79*	0.66*	0.72*	0.60*	0.93*	1			
NO_3^-	-0.30*	0.47*	0.20	0.21	0.41*	0.15	0.11	-0.29*	0.28*	0.17	0.35*	0.24	0.43*	0.41*	1		
SO_4^{2-}	0.06	0.11	0.13	0.05	0.08	-0.10	0.20	0.01	0.05	-0.06	0.22	-0.04	0.05	-0.04	0.00	1	
Cl^-	-0.61*	0.83*	0.09	0.08	0.75*	0.66*	0.29*	0.08	0.79*	0.51*	0.78*	0.71*	0.80*	0.81*	0.41*	0.01	1

EC: electrical conductivity

Table 5: Varimax rotated factor matrix for 14 physico-chemical variables[a]

Variables	Factor 1	Factor 2	Factor 3	Factor 4
pH	-0.685	0.282	0.038	-0.380
EC	0.701	-0.302	-0.037	0.519
Fe_{total}	-0.169	0.594	0.000	-0.008
Mn^{2+}	0.888	-0.036	-0.012	0.160
Zn^{2+}	0.144	0.183	0.849	0.182
Cu^{2+}	-0.131	-0.117	0.874	-0.150
Pb^{2+}	0.763	-0.198	-0.007	0.125
Na^+	0.849	-0.004	0.011	0.433
K^+	0.785	0.493	-0.020	-0.127
Ca^{2+}	0.867	0.201	0.023	0.181
Mg^{2+}	0.934	0.052	0.015	0.023
NO_3^-	0.129	0.193	0.028	0.920
SO_4^-	0.279	0.832	0.064	0.186
Cl^-	0.927	0.145	0.039	-0.045
Eingenvalue	6.77	1.71	1.42	1.19
% Variance explained	48.35	12.21	10.16	8.49
% cumulative variance	48.35	60.56	70.71	79.20

[a] marked loadings are >0.7, EC: electrical conductivity.

The higher decrease of clay contents and the increase of exchangeable-Mg^{2+} at 3.0 m depth suggest the occurrence of saprolite. Therefore, the cation exchange capability at this depth does not represent the real soil exchange capacity.

CONCLUSION

The elaboration of data indicated that the impact of tannery effluents on acid soils is notable because of a general increase of heavy metals availability, with the exception of total Cr and Fe, due to the change in soil pH after disposal.

The factor analysis allowed selecting four factors: salinity, SO_4^{2-}, Zn^{2+} and Cu^{2+} and NO_3^-. It is relevant to consider also the active role played by organic matter in the soil and active biotic components at different depths, the latter being directly involved in some enzymatic soil processes such as oxidation/reduction and nitrification activity.

We must take into account that Mn^{2+} was released in soil solution related to Mn-oxide reduction caused by Cr(III) input and pH decrease. On the other hand, chromium, the main heavy metal in the effluents, was not detected in the available forms, probably due to coprecipitation reactions of Cr and Fe and to sorption onto oxides, oxi-hydroxides and hydroxides. It is remarkable the importance of these mineral soil constituents for a reduction of Cr availability and downward migration in the soil profile.

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