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Geochemical evaluation of soils and tannery sludge from Franca region, São Paulo State, Brazil

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****(In Memoriam)*

ABSTRACT

This paper describes a geochemical study focusing on samples of soils and tannery sludge collected in the region of Franca, São Paulo State, Brazil. Geochemical analysis by X-ray fluorescence was done for both matrices to get the concentration of major oxides SiO_2, TiO_2, Al_2O_3, Na_2O, K_2O, CaO, MgO, Fe_2O_3, MnO, and P_2O_5, as well as of the trace elements Zr, Sr, Cr, Cu, Zn, Ni, Co, Ba, Rb, V, Nb, Y, La, Ce, and Ga. The loss on ignition (LOI) method was also used to provide an estimation of the organic matter (OM) content in the samples. The ternary diagram SiO_2-Al_2O_3-Fe_2O_3 allowed classification of the soil samples as kaolinized, exhibiting very high levels of SiO_2, while the tannery sludge samples presented an enhanced concentration of organic matter. The enrichment factor (EF) was calculated from the mean world concentration of the parameters analyzed in soils (Clarke value). The obtained EFs permitted the evaluation of the effects of changing the use of some chemicals during the cycle of the leather production, sometimes with positive results, but without success in other cases.

Keywords **–** soils, tannery sludge, geochemical analysis, Clarke value, Franca region, São Paulo State in Brazil

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I. Introduction

Nowadays, solid waste materials left over after wastewater treatment are a global challenge, as they may cause several environmental hazards. Among them, tannery sludge generated in leather processing plants has been extensively investigated as it typically contains high concentrations of chromium, sulfides, and other chemicals used in tanning, as well as organic matter such as hair, flesh, and fat from animal hides [1]. Due to its composition, tannery sludge is classified as hazardous waste and requires careful handling and disposal [1].

The term hide refers to a natural material composed of collagen fibers linked to a three-dimensional structure, which has been used to designate the skin of larger animals (*e.g.,* cowhide or horsehide), whereas "skin" refers to that of smaller animals (*e.g.,* calfskin or kidskin) [2]. The preservation process employed is a chemical treatment called tanning, which converts the otherwise perishable skin to a stable and non-decaying material [2]. Although the skins of such diverse animals as ostrich, lizard, eel, and kangaroo have been used, the more common leathers come from cattle [2]. Therefore, the leather is a durable and flexible material created through the tanning of putrescible animal rawhide and skin, primarily cattle hide.

Leather can be produced through different manufacturing processes, ranging from cottage industry to heavy industry. In the leather industry, the skin and rawhide are by-products of the meat industry, because the meat has greater commercial value than the rawhide and skin [3].

Ancient civilizations used leather for waterskins, bags, harnesses and tack, boats, armour, quivers, scabbards, boots, and sandals. Tanning was being carried out by the inhabitants of Mehrgarh in Pakistan between 7000 and 3300 BCE. Around 2500 BCE, the Sumerians began using leather, affixed by copper studs, on chariot wheels. The process of tanning was also used for boats and fishing vessels: ropes, nets, and sails were tanned using tree bark [4, 5].

The production of leather from cattle hides is a significant economic activity in Brazil, ranking 5th globally, after the USA, Russia, India, and Argentina [6]. However, the commercial cattle herd in Brazil is the second-largest in the world, with an estimated total of 232 million head and increasing productivity [7]. In 2019, Brazil exported approximately 179 million m^2 of hides and skins [7]. Consequently, Brazil is considered one of the largest leather exporters worldwide, producing 42 million pieces per year (10-11% of the whole global leather production), with more than half of this amount being exported to other countries, chiefly to Italy and China [8].

The number of tanneries in Brazil is about 450. São Paulo State in the country is the major exporter, reaching approximately 33.1% of the Brazilian national production [6]. Franca city and nearby at São Paulo city (Fig. 1) are the main centers dedicated to the production of leather and footwear, where a total of ~1,015 industries are installed, of which 28% are suppliers of raw materials for the production of footwear and several other leather derivatives, with the producing companies accounting for around 46% [9]. This is supported by the large number of tanneries occurring in that region, whose activities started in 1886 at the banks of the Cubatão stream [8]. This paper describes a geochemical study focusing on some tannery sludge and soil samples from that region, reporting a novel dataset and information obtained from the analysed samples.

Fig. 1. Location of Franca city in São Paulo State, Brazil.

II. The leather production cycle and wastes released

The leather manufacturing process is divided into three fundamental sub-processes [3]: 1) preparatory stages; 2) tanning; and 3) crusting.

The preparatory stages involve the hide/skin preparation for tanning, including steps of preservation, soaking, liming, unhairing, fleshing, splitting, reliming, deliming, bating, degreasing, frizing, bleaching, pickling, and depickling [3]. Figs. 2 and 3 illustrate some of these procedures for a tannery installed in the Franca region.

In the second stage, tanning, the protein of the raw hide or skin is converted into a stable material which will not putrefy, being suitable for a wide variety of end applications [3]. The main difference between raw and tanned hides is that raw hides form a hard, inflexible material after drying out, which putrefy when re-wetted [3], whereas the tanned material dries out to a flexible form that does not become putrid when wetted back [3].

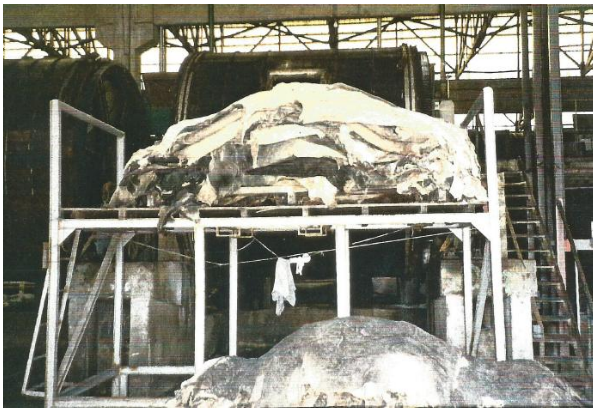

Fig. 2. Salted skins in a tannery deposit ready to begin the industrialization process in a tannery in the Franca region. According to [10].

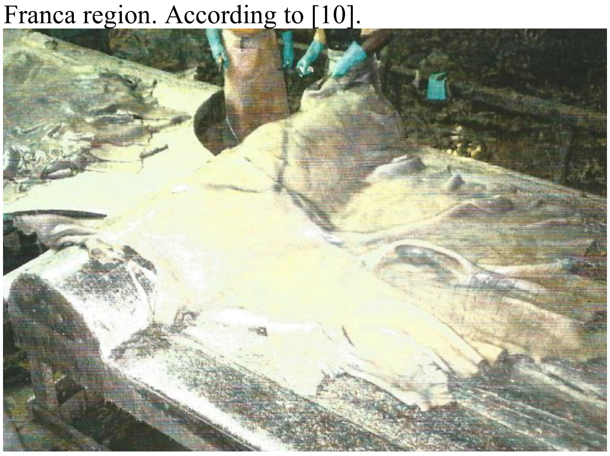

Fig. 3. Unhaired and fleshed skin, ready for splitting, in a tannery in the Franca region. According to [10].

Chromium (Cr) is the most commonly used tanning material, which leaves the leather once tanned a pale blue color (due to the chromium), being the product named “wet blue” [11], as shown in Figs. 4 and 5. The process was invented in 1858, involving the use of chromium sulfate or other salts of chromium. After finishing the pickling, the hides’ pH will typically be between 2.8 and 3.2 [11]. At this point, the hides are often loaded in a drum and immersed in a float containing the tanning liquor [3], as illustrated in Fig. 6.

The final stage, crusting, is when the hide/skin is thinned, re-tanned and lubricated (Figs. 7 and 8). Often, a coloring operation is included in the crusting sub-process. The chemicals added during crusting have to be fixed in place. The culmination of the crusting sub-process is the drying and softening operations [3]. Figs. 9-11 illustrate some of these aspects.

Fig. 4. Lowering of the “wet blue” leather in a tannery in the Franca region. According to [12].

Fig. 5. Cutting of the “wet blue” leather in a tannery in the Franca region. According to [10].

In view of the various steps involved on the leather production, such an activity exhibits high environmental impact, most notably due to 1) the impact of livestock, 2) the heavy use of polluting chemicals in the tanning process and 3) the air pollution due to the transformation process (hydrogen sulfide during dehairing and ammonia during deliming, solvent vapors).

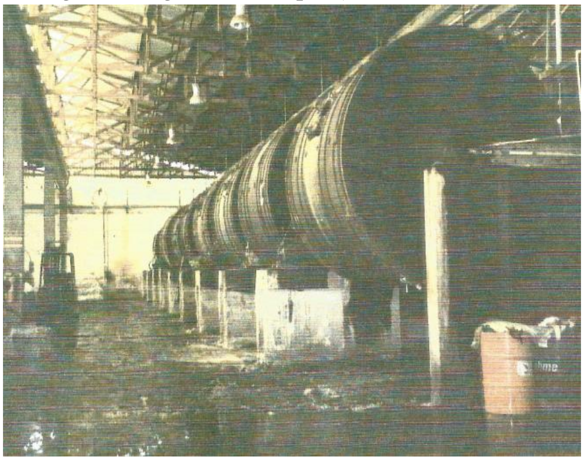

Fig. 6. Drums storing the hides/skins and tanning liquor in a tannery in the Franca region. According to [10].

Fig. 7. Re-tanning occurring in a drum during the leather industrialization in a tannery in the Franca region. According to [12].

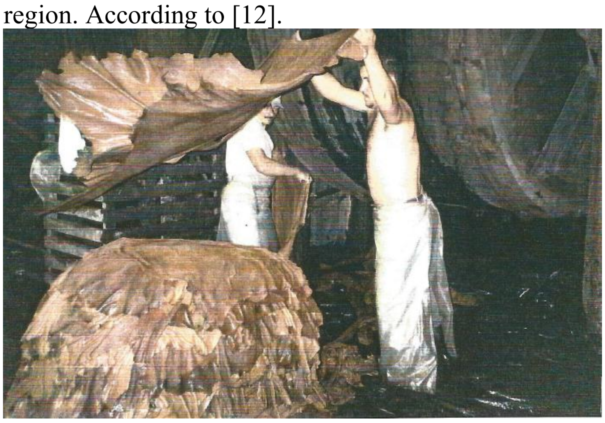

Fig. 8. Dyed leather being removed from the drum in a tannery in the Franca region. According to [10].

It has been reported that 1 ton of hide or skin generally leads to the production of 20 to 80 m^3 of turbid and foul-smelling wastewater, including chromium levels of 100-400 mg/L, sulfide levels of 200-800 mg/L, and high levels of fat and other solid wastes, as well as notable pathogen contamination [13]. Some of these releases are illustrated in Figs. 12-14.

Fig. 9. Machine for drying leather, with rubber cylinders, in a tannery in the Franca region. According to [10].

Fig. 10. Leather drying in a warehouse from a tannery in the Franca region. According to [12].

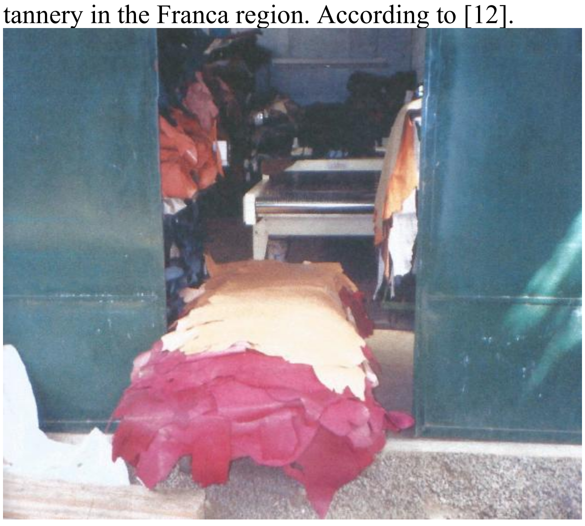

Fig. 11. Final finishing of the leather production in a tannery in the Franca region. According to [12].

Additionally, pesticides are also often added for hide conservation during transport. The solid wastes represent up to 70% of the wet weight of the original hides, implying that the tanning process comes at a considerable strain on water treatment installations [13]. The recovered effluents may be stored in aeration ponds for treatment, as shown in Fig. 15, for example. Therefore, the wastewater stream of the corresponding industrial plants suffers physicochemical and biological treatment, generating the tannery sludge that is finally dried in tanks, which is ready for a decision about its final disposal, as illustrated in Fig. 16.

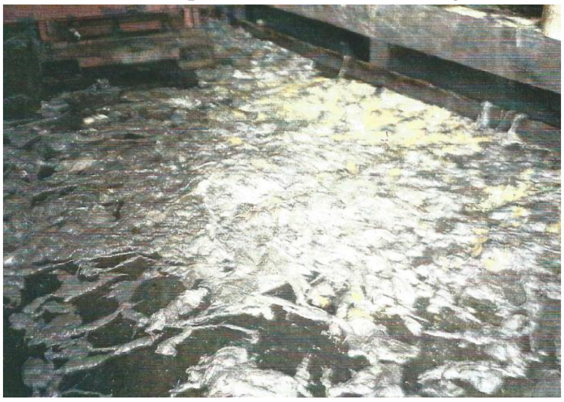

Fig. 12. Fleshing residue during the leather production in a tannery in the Franca region. According to [10].

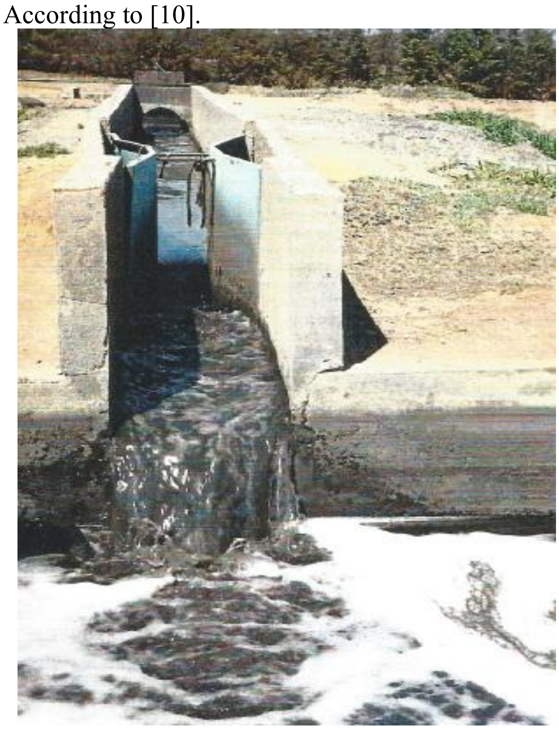

Fig. 13. Channel receiving effluents generated during the leather production in tanneries in the Franca region. According to [10].

Fig. 14. Pipe discharging effluents generated during the leather production in tanneries in the Franca region. According to [10].

Fig. 15. Aeration pond receiving the effluents generated during the leather production in tanneries in the Franca region. According to [10].

Fig. 16. Sludge drying tank in a tannery in the Franca region. According to [12].

The solid wastes generated, mainly in the shaving and cutting stages, are classified as Class I dangerous according to the Brazilian standards ABNT NBR 10.004 and ABNT NBR 10.005, due to their toxicity [14]. It has been estimated that each piece of tanned leather results in 2 to 3 kg of chromium-tanned shavings, implying about 375 tons of solid tannery wastes generated daily in Brazil [14].

In many tanneries occurring elsewhere, the processes and problems are similar to those described here, resulting in contaminated solid wastes that require measures to avoid hazards to the environment. For instance, in the Indian city of Kanpur ("Leather City of the World") on the banks of the Ganges River, with 3 million inhabitants, the census of 2011 indicated 10,000 tanneries, causing so high pollution levels that the pollution control board decided to shut down 49 high-polluting tanneries out of 404 in July 2009 [15].

Therefore, nowadays the tannery sludge is a great challenge for researchers because it can have severe environmental consequences to soil, water, and air, if not properly treated/managed as pointed out by [1] and summarized here: 1) the application of untreated sludge to agricultural land can lead to the accumulation of heavy metals in the soil, affecting crop growth and contaminating the food chain; 2) the improper disposal of tannery sludge can lead to harmful chemicals leaching into groundwater and surface water, posing risks to aquatic ecosystems and drinking water sources; 3) the incineration of tannery sludge without adequate pollution control measures can release toxic gases, including dioxins and furans, into the atmosphere.

Effective treatment of tannery sludge is crucial to minimize its environmental impact, for instance, by chemical stabilization (addition of lime or other alkaline materials to the sludge to reduce its toxicity), biological treatment (use of microorganisms to degrade the organic matter in tannery sludge), thermal treatment (heating the sludge to high temperatures to destroy organic pollutants and reduce the waste volume), and/or paddle dryer + drying (agitation of the sludge with heated paddles to promote efficient heat transfer and drying of the material) [1].

After drying, tannery sludge has been repurposed in some different ways, aiming to reach a more sustainable approach to waste management [1]:

1) dried sludge as fuel source as the organic content in the sludge, once dried, can be combusted to produce energy; 2) dried sludge as a raw construction material (bricks, cement, and concrete); 3) dried sludge as a soil amendment to improve soil fertility and structure. Examples of these applications in the literature are given by [14, 16-22]. Among these possibilities, some efforts have been made to verify the potential use of tannery sludge from the Franca region as a soil amendment, as also reported in this paper.

III. Study area

The city of Franca is 401 km distant from São Paulo city, the capital of São Paulo State, being located at a latitude of 20°32'03" S, a longitude of 47°24'38" W, and at an altitude of 1040 m (Fig. 1). Geologically, the region of Franca is inserted within the northeastern edge of the Paraná sedimentary basin (PSB), presenting rocks from the Permo-Carboniferous to the Upper Cretaceous, including the flows of basic rocks intruded into the sedimentary package, and also Neocenozoic sediments capping the surfaces [23].

Lima [24] characterized the region of Franca as having the following geological substrates: Cenozoic covers (fine, coarse, coarse conglomeratic sandstone, siltstone, and conglomeratic siltstone – Itaqueri Formation); Bauru Group (sandstones – Marília Formation); São Bento Group (sandstones – Pirambóia Formation; silicified sandstones – Botucatu Formation; basalts and diabases – Serra Geral Formation). The dominant presence corresponds to the Itaqueri and Serra Geral Formations, which occur in associated forms [24].

The city of Franca is well drained, being crossed by the Canoas River to the northeast, Macaco and Pouso Alto streams to the north, Salgado stream to the northwest, Sapucaí River to the south, and Macaúbas stream to the southeast [24]. The most important water body to the region is the Sapucaí River, which possesses the largest water volume [24].

The Franca's region climate is classified as Tropical High Altitude, according to the Köppen system, characterized by dry winters and rainy summers [23]. The wet season occurs between October and March, whilst the dry period occurs between April and October [10]. The mean annual temperature is about 23°C, generally ranging between 13°C and 30°C [10]. The average rainfall is 1370 mm/year, with a range of 1100-1500 mm [10].

The vegetation types found in the Franca's region are as follows [23]: Cerrado (1,267.2 ha), Seasonal Forest (2,262.4 ha), Secondary Forest (364.2 ha), Riparian vegetation (7,266 ha), and reforestation with eucalyptus (33.1 ha).

The soils present in the municipality and region of Franca are [23]: red latosols (purple latosol and dark red latosol); red-yellow latosols; dystroferric and eutroferric, moderate A, with clayey texture; dystrophic and moderate A, and quartzarenic neosols (quartz sands and hydromorphic quartz sands).

IV. Sampling and Analysis

In this study, two samples of soil (SO1= 0-20 cm depth; SO2= 20-40 cm depth) and two samples of tannery sludge (TS1= December 2018; TS2 = June 2019) were collected in the region of Franca for chemical analysis.

Both matrices were analyzed by the X-ray fluorescence (XRF) technique, utilizing the pressed powder method and one WDXRF (wavelength dispersive X-ray fluorescence) spectrometer (Philips PW 2400) that operates at 60 kV, 125 mA, and 3 kW of maximum voltage, current, and power, respectively, with the need for external cooling [25]. The spectrometer is installed at LABOGEO-Geochemistry Laboratory, DG- Geology Department, IGCE-Geosciences and Exact Sciences Institute, UNESP-São Paulo State University, Rio Claro city, São Paulo State, Brazil.

The basic operation concept consists of a source, the sample, and a detection system, as detailed by [26, 27]. The Kα lines energies of the major elements are [28]: Si (1.7 keV), Al (1.5 keV), Na (1 keV), K (3.3 keV), Ca (3.7 keV), Mg (1.3 keV), Fe (6.4 keV), Mn (5.9 keV), Ti (4.5 keV), and P (2.0 keV).

The samples were crushed to <74 μm in a vibration disk mill. The powder (~8g) was mixed with Oregon CAS9002-88-4 wax (~1.5g) as a binding agent and boric acid (H_3BO_3) (~3.5g) for standing the mixture that was pressed into a pellet press. Such a procedure yielded a 40-mm diameter disc submitted to XRF analysis in the spectrometer, which was previously calibrated with certified reference materials. The Semi-Q software allowed the data acquisition into the spectrometer [25].

The loss on ignition (LOI) method was also used to provide an estimation of the organic matter (OM) content in the samples, as LOI is related to the presence of OM, carbon dioxide (CO_2) (of carbonates), sulfur dioxide (SO_2) (of sulfides), adsorbed water (H_2O), and H_2O retained in crystal lattices and fluid inclusions [29]. For LOI evaluation, 1 g of each sample was inserted into a crucible, then placed into a muffle at ~500°C for 2 h and weighed again to determine the weight difference (in percentage) after firing [30].

V. Results and Discussion

The results obtained in the XRF readings are reported in Tables 1 and 2. The first aspect to be highlighted from the analytical data of the soil samples is the accentuated presence of SiO_2 in their composition (mean of 93.8%). A ternary SiO_2-Al_2O_3-Fe_2O_3 diagram was proposed by [31] to investigate the presence of ferrite, bauxite, and kaolin in soil profiles, in which the mean values reported in Table 1 were plotted, as shown in Fig. 16. Such a diagram emphasizes that the soils analyzed suffered intense kaolinization processes that occur by supergene autochthonous weathering and hydrothermal alteration, which are typically prevalent in pluvial, wet and dry (savannah) tropical climate [32].

Table 1. Results of the XRF measurements for the soil samples collected in the Franca region.

Parameter	Unit	Sample SO1	Sample SO2	Mean
SiO_2	%	93.90	93.79	93.84
TiO_2	%	0.26	0.27	0.27
Al_2O_3	%	2.55	2.56	2.56
Na_2O	%	0.08	0.05	0.06
K_2O	%	0.04	0.02	0.03
CaO	%	0.05	0.08	0.06
MgO	%	0.01	0.01	0.01
Fe_2O_3	%	0.97	1.05	1.01
MnO	%	0.01	0.01	0.01
P_2O_5	%	0.04	0.03	0.03
LOI	%	2.15	2.18	2.16
Zr	ppm	189	217	203
Sr	ppm	<10	<10	<10
Ba	ppm	28	23	25.5
Cu	ppm	1	1	1
Zn	ppm	<5	<5	<5
Ni	ppm	<5	<5	<5
V	ppm	22	23	22.7
Co	ppm	8	6	7
Cr	ppm	<10	<10	<10
Rb	ppm	<5	<5	<5
Y	ppm	1	1	1
Nb	ppm	5	7	6
La	ppm	15	8	11.6
Ce	ppm	16	23	19.6
Ga	ppm	11	12	11.2

Soil weathering indices Ki and Kr have been utilized to compare how much Si is mobile relatively to Al and Fe which often exhibit lower mobility in soil profiles [33, 34]. They are calculated by the following equations [34]: Ki= 1.7 (SiO_2/Al_2O_3) and Kr= [(SiO_2/0.6)/ (Al_2O_3/1.02)] + (Fe_2O_3/1.6). Values equal to or lower than 2 indicate advanced stages of weathering, while values higher than 2 suggest incipient weathering stage. Rough estimation of these indices from data reported in Table 1 indicate Ki=62.4 and Kr=63, suggesting that the soils analyzed are non-lateritic.

Table 2. Results of the XRF measurements for the tannery sludge samples collected in the Franca region.

Parameter	Unit	Sample TS1	Sample TS2
SiO_2	%	11.63	15.59
TiO_2	%	0.19	0.35
Al_2O_3	%	1.0	1.48
Na_2O	%	0.95	4.59
K_2O	%	0.06	0.12
CaO	%	23.12	64.80
MgO	%	1.97	4.54
Fe_2O_3	%	0.82	1.33
MnO	%	0.01	0.03
P_2O_5	%	0.56	1.03
LOI	%	59.7	6.10
Zr	ppm	65	1.48
Sr	ppm	1079	372
Ba	ppm	38	<10
Cu	ppm	<5	159.5
Zn	ppm	22	402
Ni	ppm	<5	<5
V	ppm	1	<1
Co	ppm	3	<1
Cr	ppm	158	0.87*
Rb	ppm	<5	<5
Y	ppm	1	<1
Nb	ppm	1	<1
La	ppm	1	<1
Ce	ppm	17	<1
Ga	ppm	5	<1

*measured by spectrophotometry

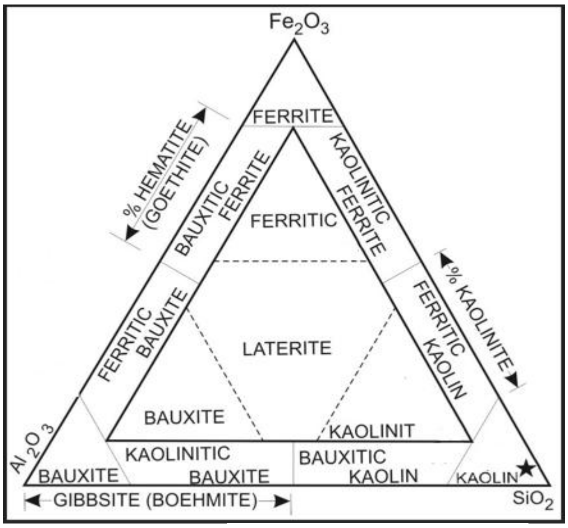

Fig. 16. Ternary SiO_2-Al_2O_3-Fe_2O_3 diagram as proposed by [31] with insertion of the mean composition obtained for the soils analyzed in this study.

The analytical data reported in Table 2 highlight a lower SiO_2 concentration compared to that of CaO and organic matter (LOI) in the tannery sludge sample TS1, which is related to some steps involved in the leather production. Chromium in this sample corresponded to 158 ppm, which is lower than other reported values in the study area, for instance, 1,805 ppm and 10,800 ppm [35]. However, the Cr concentration in sample TS1 is still higher than the mean global Cr concentration in soils (75 ppm, Table 3) and, for its reduction, some changes were introduced in the reagents previously utilized for promoting neutralization of the wastewaters, which implied on a lower Cr concentration in the novel sample (TS2), corresponding to 0.87 ppm (Table 2). Table 2 shows that, beyond Cr, other constituents also exhibited a significant difference in the new concentration value, for instance, CaO (increased from 23.12% to 64.8%), MgO (increased from 1.97% to 4.54%), LOI (decreased from 59.7% to 6.1%), etc.

The average crustal concentration has been named Clarke, remembering the American geochemist Frank W. Clarke, who conducted extensive chemical analysis of rocks at the USGS between 1889 and 1924 [36]. The same concept of Clarke to crustal rocks may be applied to the pedosphere, but now considering the global mean concentration of constituents in soils. However, this is a challenge for researchers due to the complex interactions between the soil and parent material, physicochemical properties of the soil, and possible exogenous inputs from agriculture or industry [37]. Table 3 reports the Clarke values of the constituents analysed in this study as reported by [38-40], their mean value, and the dimensionless enrichment factor (EF) calculated by the ratio of the concentration of the constituent (Tables 1 and 2) to its mean Clarke value.

The EF1 values shown in Table 3 indicate that, except for SiO_2, the kaolinized soils of the Franca region are impoverished in the remaining constituents analyzed, with the lowest value corresponding to MgO (0.008).

The EF2=2.1 for Cr in the sample TS1 indicated enrichment of the tannery sludge relative to the Clarke value, which also occurred for other constituents like CaO (11.3), MgO (1.71), P_2O_5 (3.2), and Sr (4.4).

The renewed chemical neutralization treatment adopted for the wastewaters generated during the leather production implied lowering the Cr concentration relative to the Clarke value, i.e., the EF decreased from 2.1 in sample TS1 to 0.01 in sample TS2. Contrarily, other constituents exhibited increasing EF values, the most accentuated corresponding to Na_2O (from 0.94 to 4.54), CaO (from 11.3 to 31.6), MgO (from 1.71 to 3.95), P_2O_5 (from 3.20 to 5.88), Cu (0.17 to 5.32), and Zn (0.27 to 5.02).

Table 3. Clarke values in % for major constituents (oxides) and in ppm for trace elements, as well as the enrichment factor (EF) calculated from the dataset reported for the samples collected in the Franca region (Tables 1 and 2).

Parameter	Clarke 1 [38]	Clarke 2 [39]	Clarke mean	EF1[1]	EF2[2]	EF3[3]
SiO_2	59.9	70.6	65.2	1.48	0.18	0.24
TiO_2	0.67	0.83	0.75	0.36	0.25	0.47
Al_2O_3	15.1	13.4	14.2	0.18	0.07	0.10
Na_2O	1.35	0.67	1.01	0.06	0.94	4.54
K_2O	1.7	1.7	1.7	0.02	0.04	0.07
CaO	2.0	2.1	2.0	0.03	11.3	31.6
MgO	1.5	0.8	1.2	0.008	1.71	3.95
Fe_2O_3	5.0	5.7	5.4	0.19	0.15	0.25
MnO	0.07	0.13	0.10	0.10	0.12	0.30
P_2O_5	0.17	0.18	0.18	0.20	3.20	5.88
Zr	230	400	315	0.64	0.20	0.005
Sr	240	250	245	0.04	4.4	1.5
Ba	500	500	500	0.05	0.08	0.02
Cu	-	-	30 [40]	0.03	0.17	5.32
Zn	70	90	80	0.06	0.27	5.02
Ni	20	50	35	0.14	0.14	0.14
V	90	90	90	0.25	0.01	0.01
Co	10	8	9	0.78	0.30	0.11

Cr	80	70	75	0.13	2.10	0.01
Rb	65	150	107.5	0.05	0.05	0.05
Y	20	40	30	0.03	0.03	0.03
Nb	12	10	11	0.51	0.09	0.09
Ce	65	50	57.5	0.34	0.29	0.02
Ga	-	20	20	0.56	0.24	0.05

$EF1^1$=mean soil/mean Clarke; $EF2^2$=sample TS1/mean Clarke; $EF3^3$=sample TS2/mean Clarke

Therefore, the EF is a helpful parameter to evaluate the use of the tannery sludge as a soil amendment. It indicates the feasibility of the adopted procedures during the whole cycle of the leather production. Despite the benefits due to the addition of organic matter and phosphorus, as well as the reduction of chromium, the risks of increasing the soil salinity and introduction of other pollutants are adverse effects revealed by the enhanced levels of Na_2O, CaO, MgO, Cu, and Zn found in the study area. Also, further investigations are envisaged to evaluate the adsorption capacity of contaminants by the kaolinized soils occurring in the study area and elsewhere.

VI. Conclusion

The tannery sludge is a by-product of leather production, presenting environmental challenges due to its high content of chromium, ammonium, organic nitrogen, salinity, and sulfide, potentially leading to soil contamination. On the other hand, the tannery sludge also offers opportunities for resource utilization, for instance, as a fuel source due to the organic content in the sludge, as a raw construction material, or as a soil amendment. Several of these applications have been described in the literature; however, in Brazil, the main recorded experiences refer to the use in agriculture, for example, to examine the effects of applying tannery sludge as fertilizer in the sugarcane crop. This study focused on the Franca city and vicinity in the Brazilian State of São Paulo, which is the main center dedicated to the production of leather and footwear in the country. Samples of soils and tannery sludge were collected at that site and subjected to X-ray fluorescence analysis, which is a very traditional technique utilized in Earth Sciences, chiefly for determining the composition of rocks and soils. The dataset obtained revealed that the soils are dominated by kaolinization processes and that the tannery sludge initially exhibited a Cr concentration value above the mean world concentration in soils. However, after modification in the chemicals utilized in some industrial steps of the leather production, the Cr concentration in the wastewaters was reduced, decreasing its level in the sludge. In contrast, other constituents such as Na_2O, CaO, MgO, Cu, and Zn increased in the tannery sludge, claiming for attention due to possible risks of salinization and contamination of the soil covers. These findings showed the usefulness of the adopted enrichment factor for the geochemical data treatment, suggesting its use in future investigations focusing on this research topic elsewhere.

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