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Validation of a Standard Operating Procedure (SOP) for Forensic Soils Investigation in Brazil

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ABSTRACT: Soil traces are useful as forensic evidence due to their potential to transfer and adhere to different types of surfaces on a range of objects or persons. Several works have been developed in forensic soils, under different analytical approaches. However, in Brazil, only the researches from the Group of the Federal University of Paraná have developed works with soils under a forensic approach. Focus has been given on the sequential chemical analyses and mineralogical techniques once they presented a large potential to discriminate soil samples, even that originated from the same bedrock. In this way, this work aimed to test a Standard Operating Procedure (SOP) for forensic soil sampling and an analytical protocol in Brazil between the academy and the scientific police through a blind simulated crime scene scenario. Samples were collected at four sites located in the Curitiba Metropolitan Region. All soils were classified as Inceptisol (*Cambissolo*), and the parent material in Curitiba is claystone and in Colombo is limestone. Around 3 g of sample composed by silt + clay fraction were isolated and analyzed by sequential chemical procedure: i) extraction of poorly ordered iron and aluminum oxides with ammonium oxalate (AO); ii) extraction of crystalline iron oxides with sodium dithionite-citrate-bicarbonate (DCB); and iii) extraction of poorly ordered aluminosilicates and gibbsite with NaOH 0.5 mol L^{-1}. All data were transformed by square root and formed a data matrix subsequently analyzed in a principal component analysis (PCA). Most of the samples were properly grouped according to their provenance at all four sites tested, showing the potential of the Standard Operating Procedure (SOP) in a real crime scene. The sampling procedures presented in the SOP were detailed enough to allow the appropriate police work in forensic cases in any part of Brazil. As future considerations, modifications to the sample treatment and analytical protocol could be made depending on the context of the forensic work. Intense anthropogenic activities, such as domestic waste disposal in urban areas, would potentially reduce the discrimination power of such a proposed chemical analytical protocol.

Keywords: forensic science, soil evidence, sequential chemical analysis, gibbsite, iron oxides.

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INTRODUCTION

In forensic science, soil can be a powerful contact trace material as it can serve to test a link of a potential source of the soil with an item on which it is found. Its potential as evidence in crime scenes is due to its often highly individualistic nature, which results in a vast diversity and complexity, enabling it to be distinguished between soil samples (Farrugia et al., 2012; Dawson and Mayes, 2015; Finley et al., 2015; Woods et al., 2016; Demanèche et al., 2017). In addition, soil has a large probability to transfer and retention (mainly the small fractions such as clay, silt, and associated organic matter), and it is expected that the suspect does not dispense much attention to the potential soil traces adhered in objects related to a crime (Fitzpatrick, 2013).

Soil traces can easily be visualized and collected in crime scenes, and a range of combined analytical techniques can be applied to characterize them. For a soil of unknown origin, the choice of method will depend on the aspects such as amount, condition, and the predominant fraction of the sample, as well as the equipments and time available (Marumo, 2003; Dawson and Hillier, 2010). In Brazil the partner between the Department of Soil Science & Agricultural Engineering of the Federal University of Paraná (UFPR) and the State and Federal Scientific Police allowed substantial advance in the establishment of the chemical, physical, and mineralogical protocol of analyses to investigate soil traces (Melo et al., 2008; Prandel et al., 2017; Corrêa et al., 2018; Melo et al., 2018).

Laboratory analyses are only efficient in the characterization of the samples if the soil traces are appropriately sampled at the crime scene and subsequently follow a rigorous procedure of sampling and handling (Fitzpatrick, 2011; Fitzpatrick and Raven, 2012; Wald, 2015; Fitzpatrick and Raven, 2016). In Brazil, there is an emergent need to standardize the soil sampling, and adjust the police sampling with the sampling carried out by the academic/scientific research. Until recently, soil residues in crime scenes which occurred in Brazil have been largely ignored by the criminal experts due to the unavailability of standard procedures for soil sampling, both for the object/victim and the suspect.

To improve the lack of procedures for soil sampling and to allow an efficient comparison and discrimination among the soil samples collected in forensic caseworks, a Standard Operating Procedure (SOP) was developed in Brazil. The SOP was created by Researchers of the Department of Soil Science & Agricultural Engineering from the Federal University of Paraná (UFPR) for application in the routine work of the State and Federal Police from Brazil. The final step for the wider use of the SOP by the scientific police from Brazil requires a test and calibration of the soil sampling procedures.

This work aimed to develop and test a Standard Operating Procedure (SOP) for forensic soil sampling in Brazil between the academy and the scientific police through a simulated crime scene test scenario. To verify the compatibility of the soil sampling, it was used chemical, physical, and mineralogical data from the soil samples using the sequential protocol of analyses previously developed and validated in the same region for forensic purposes by Melo et al. (2008). Those authors were able to separate soil trace samples (1.0 g) collected in areas developed under the same parent material located in different neighbourhoods, as well grouped soil samples from the same neighbourhood (samples were separated away from each other at a distance of 2.0 m) in Colombo and Curitiba, Paraná State, Brazil. The hypothesis of the present work is that the samples collected by the academy and Federal Police form homogenous groups related to their physical, chemical, and mineralogical properties when sampled from the same site (neighborhood). Such similarity of groupings certifies that the police practitioners are able to follow the soil sampling procedures established by the academy in the SOP and the analytical protocol developed by Melo et al. (2008) present high potential to be applied in forensic case works.

MATERIALS AND METHODS

Simulated crime scene and soil traces sampling

A mock crime scene was designed in June 2017 in two neighborhoods from the urban areas in Curitiba (Santa Candida and Boa Vista) and Colombo (Guaraituba and Guarani), Paraná State, Brazil (Figure 1). All sites belong to the Curitiba Metropolitan Region and are away from each other by a distance of 2 to 4 km. Rates of crimes are generally higher in urban and inner-city areas compared to in rural areas (Gibbs and Haldenby, 2008). The sites were located on both similar and contrasting parent material (Table 1) to test the reliability within and between comparisons. All soils were classified as Inceptisol according to U.S. Soil Taxonomy (Soil Survey Staff, 2010) and as *Cambissolo Háplico* according to Brazilian Soil Classification System (Santos et al., 2013).

The occurrence of a crime was simulated in each one of the four neighborhoods from both Colombo and Curitiba. Soil samples were impregnated on the sole of the boot through a simulation of a suspect walking over a crime scene (at the central position of figure 1 in each location). Soil trace samples on the sole of the boot were collected in 3 or 4 replicates according to the site of impregnation (toe and heel positions on the sole of the boot) (Figure 2). At the moment of the impregnation, the soil was wet, which allowed the impregnation of a large quantity of soil vestige on the sole of the boot (Figure 2). All procedure for sampling in unfavorable situations of little soil vestige impregnation on the tools of the suspect is presented in the SOP.

From the site of the muddy boot (central point in a frame), four points were chosen at positions around that central position, in each corner of a square with 1.5 m apart (Figure 1). The soil sampling on the sole of the boot and from the four positions around from the muddy boot central position aimed to compare the soil sampling procedures between the academy and the criminal experts, carried out on the suspect (simulated by the sole of the boot) and in the crime scene (repetitions in the frame).

The soil sampling followed all procedures established in the Standard Operating Procedure (SOP) prepared by the researchers from the Department of Soil Science & Agricultural Engineering - UFPR. This SOP will be published after this validation. Samples from each corner of the frame were collected from 0.00 to 0.05 m of depth, using a stainless steel spatula, carefully sterilizing the tool between replicate sampling. All samples from the frame and the boot were placed in sterilized plastic flasks of 30 mL (packed individually), commercialized for laboratory exams.

Researchers proceeded to soil sampling alone without the police being present and identified the samples according to the nature and site (samples from 1 to 28; Table 1). In addition, the police followed the same sampling procedure without the presence of the researchers, following only the sampling protocol from the SOP. The identification of the samples made by the experts was blind (sample 29 to 52; Table 1), which means that during the laboratory and statistical analyses the origin of the samples collected by the police was not known.

Soil sample preparation

Samples were dried at 40 °C, hand ground, and sieved at 2 mm to remove large stones and vegetation fragments. Sample homogenization was obtained using a plastic cone and quartered, and the partition was positioned to obtain 3 g of each sample. Even considering such a worst scenario when the amount of soil sample does not perpass 1 g of soil, in this work we decided to use 3 g of soil sample. This amount was considered in relation to the available samples both by academic and police sampling. The use of a higher amount was also possible due the environmental conditions, which presented humidity high enough to improve the adherence of the soil on the sole of the boot

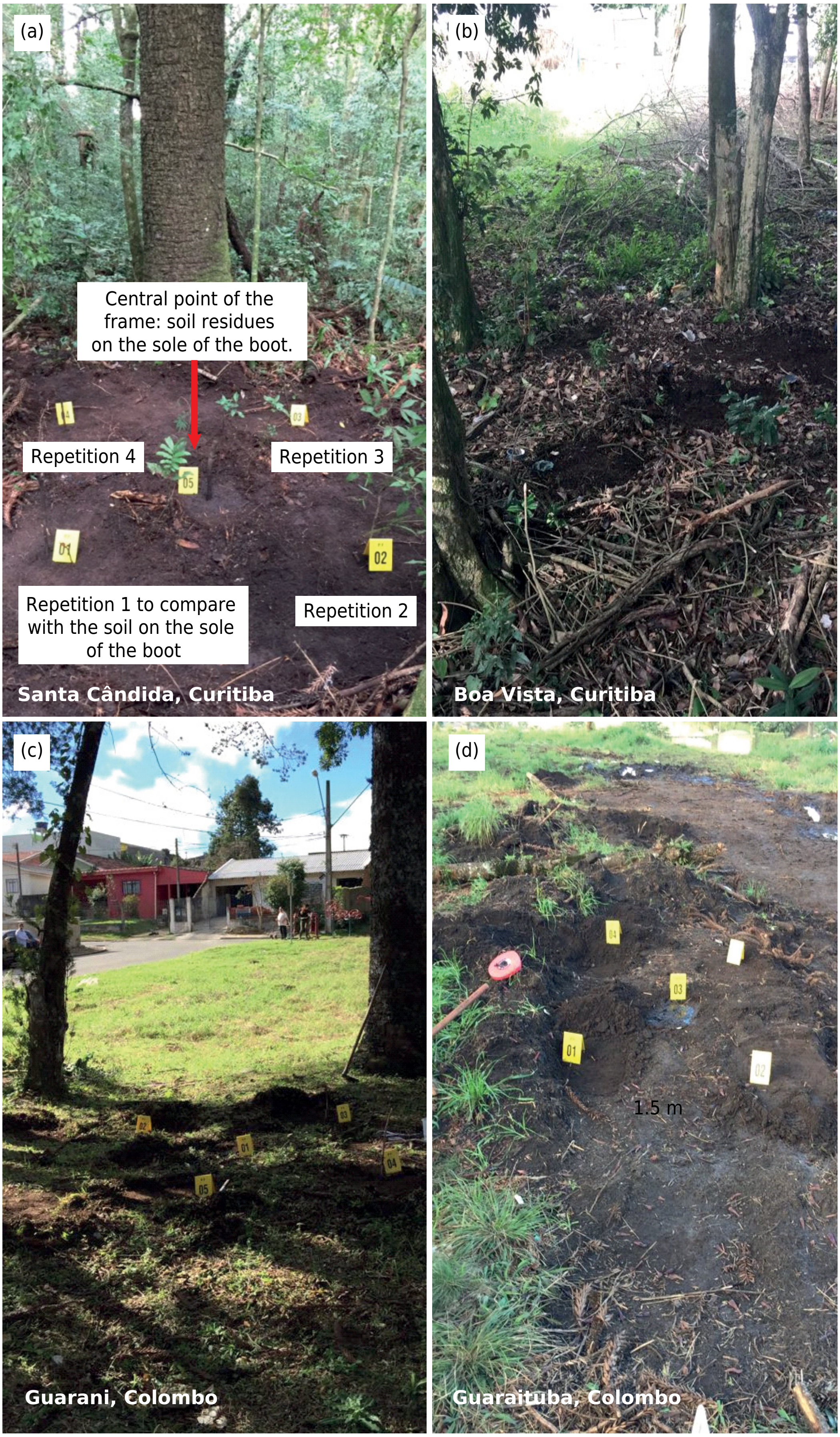

Figure 1. Sampling locations within Curitiba and Colombo, State of Paraná, Brazil. Photographs taken with markers at each of the four sampling positions carried out in a frame with a central point (sole of the boot) located in four separate urban areas, Santa Cândida - Curitiba (a), Boa Vista - Curitiba (b), Guarani - Colombo (c), Guaraituba -Colombo (d).

Table 1. Description of the sampling site.

Sample	Position	Neighbourhood	Layer	Altitude	UTM (22J)		Bedrock
					E-W	N-S	
			m				
			Site 1				
1	Frame	Santa Cândida	0.00-0.05	937	678,203 W	7,192,226 S	Claystone
2	Frame		0.00-0.05				
3	Frame		0.00-0.05				
4	Frame		0.00-0.05				
5	Heel						
6	Heel						
7	Toes						
			Site 2				
8	Frame	Guarani	0.00-0.05	924	682,747 W	7,192,633 S	Limestone
9	Frame		0.00-0.05				
10	Frame		0.00-0.05				
11	Frame		0.00-0.05				
12	Heel						
13	Heel						
14	Toes						
			Site 3				
15	Frame	Guaraituba	0.00-0.05	910	683,189 W	7,195,492 S	Limestone
16	Frame		0.00-0.05				
17	Frame		0.00-0.05				
18	Frame		0.00-0.05				
19	Heel						
20	Heel						
21	Toes						
			Site 4				
22	Frame	Boa Vista	0.00-0.05	925	676,186 W	7,190,193 S	Claystone
23	Frame		0.00-0.05				
24	Frame		0.00-0.05				
25	Frame		0.00-0.05				
26	Heel						
27	Toes						
28	Heel						
			Samples collected by Federal Police				
29	2 γ						
30	3 δ						
31	4 π						
32	5 ρ						
33	6 β						
34	7 σ						
35	8 α						
36	10 β						
37	11 σ						
38	12 ρ						
39	13 δ						

Continue

Continuation

40	14 φ
41	15 α
42	16 π
43	17 α
44	20 ρ
45	21 γ
46	22 β
47	24 σ
48	25 π
49	28 δ
50	29 ρ
51	30 σ
52	32 β

Note: heel and toe samples are trace samples, collected at the centre of the sampling frame. Santa Cândida and Boa Vista are neighborhoods from Curitiba (state of Paraná), Guarani and Guaraituba are neighbourhoods from Colombo (Curitiba Metropolitan Region).

Figure 2. Soil residues adhered on the sole of the boot used in the simulated crime scene showing the sites of sampling in repetitions on the toes and heel areas.

(Figure 2). Samples were macerated with a rubber baton and dispersed into a Na_2CO_3 0.1 g L^{-1} solution (pH 10) and sieved at 0.053 mm sieve to separate the sand fraction. Suspensions containing silt, clay, and organic matter particles were collected in porcelain capsules. This step was repeated until the water after maceration was clear. The fractions <0.053 mm (silt, clay, and organic matter) were weighed and quantified after drying. The exclusion of the sand fraction in the sequential analyses (Figure 3) was due to the reduced amount of sample available in this work. The presence of sand can reduce the sample homogenization, and it is the finer particles (silt and clay) which are preferentially adhered on shoes, tires, clothes, etc. (Fitzpatrick, 2009). Besides these aspects, we must consider that the smaller fractions, especially the colloid-size particles, are dominated by the clay minerals, humic substances, and iron, aluminum, and manganese oxi-hydroxides, which are important compounds to be considered and further investigated using sequential chemical extractions.

Removal of organic matter

Samples composed of silt+clay+organic matter were homogenized with 30 % (v/v) of H_2O_2 in 70 °C water bath to remove the organic matter fraction. Then, soil samples were oven-dried at 40 °C for 24 h.

Chemical and mineralogical analyses

The analytical methods were separated into destructive and non-destructive (Melo et al., 2008). Samples from non-destructive analyses were re-used in the subsequent procedures.

Sequential extractions

Subsamples (silt + clay) were submitted for sequential extractions according to the methodology proposed by Melo et al. (2008) (Figure 3). For all extractions (ammonium oxalate, sodium dithionite-citrate-bicarbonate, and NaOH 0.5 mol L^{-1}) the following procedures were applied: i) previously each extraction the samples were oven-dried (for 24 h) at 40 °C, grounded and sieved at 0.2 mm in order to reduce the particles size, improve the surface reactivity and increase the efficiency of the extractions; ii) subsequently each extraction, samples were washed with $(NH_4)_2CO_3$ 0.5 mol L^{-1} and deionized water, using 50 and 20 mL per washing, respectively, to remove the excess salt; iii) after washing, the samples were dried at 40 °C for 24 h, and the final mass was determined; iv) extracts were obtained by centrifugation (3,000 rpm for 10 min), and element levels (Fe, Al, As, Ba, Ca, Cd, Cr, Cu, K, Mg, Mn, Ni, P, Pb, S, Si, V, Zn, and Mo) were determined by inductively coupled plasma optical spectrometry (ICP-OES).

Extraction of low crystallinity Fe and Al oxides

The first step of the sequential extractions was performed with ammonium oxalate (AO) to determine the poorly crystallized Fe, Al, and Si forms (short-range order minerals) (Figure 3) using 0.8 g of soil sample (silt + clay) and 20 mL of 0.2 mol L^{-1} ammonium oxalate at pH 3.0, in the dark (McKeague, 1978).

Extraction of crystalline Fe oxides

Samples were recovered and the crystalline iron oxide extraction was proceeded with sodium dithionite-citrate-bicarbonate (DCB) method (Figure 3) (Mehra and Jackson, 1960). Powdered samples of 0.6 g were disposed in 100 mL tubes and subjected to the extraction three times with 9.6 mL of a solution of sodium citrate 0.3 mol L^{-1} + 1.2 mL of a solution of sodium bicarbonate 1.0 mol L^{-1} + 0.24 g of sodium dithionite. Samples in solution were manually agitated while heated at 70 °C in a water bath for 30 min.

Extraction of low crystallinity aluminosilicates and gibbsite

A mass of 0.35 g was used in the last sequential analysis for the extraction of poorly ordered aluminosilicates and gibbsite (short-range order γ-$Al(OH)_3$, Al-O-Si layers, and Si-O (opaline silica) resistant to the previous ammonium oxalate extraction) with boiling NaOH 0.5 mol L^{-1} (Figure 3) (Jackson et al., 1986; Melo et al., 2002). Samples were disposed in tubes with 2 mL of NaOH 0.5 mol L^{-1} without heating and were homogenized and moistened with that initial solution. After that, teflon beckers containing 15 mL of the NaOH 0.5 mol L^{-1} solution were placed in a sand bath at 200 °C until it boiling; the solution was then added to the tube with the samples. The boiling solution remained in contact with the sample for three minutes under constant manual agitation. Immediately after, samples were cooled in a recipient with cool water and then centrifuged.

Thermogravimetric analysis (TGA)

An amount of 10 mg of each sample previously extracted with DCB (Figure 3) was used to thermogravimetry analysis to obtain the TG diagrams. Samples were heated from room temperature to 950 °C at 10 °C min s^{-1} and gas flux of 50 mL min^{-1}, under N_2 atmosphere. Contents of kaolinite (Kt) and gibbsite (Gb) were obtained considering

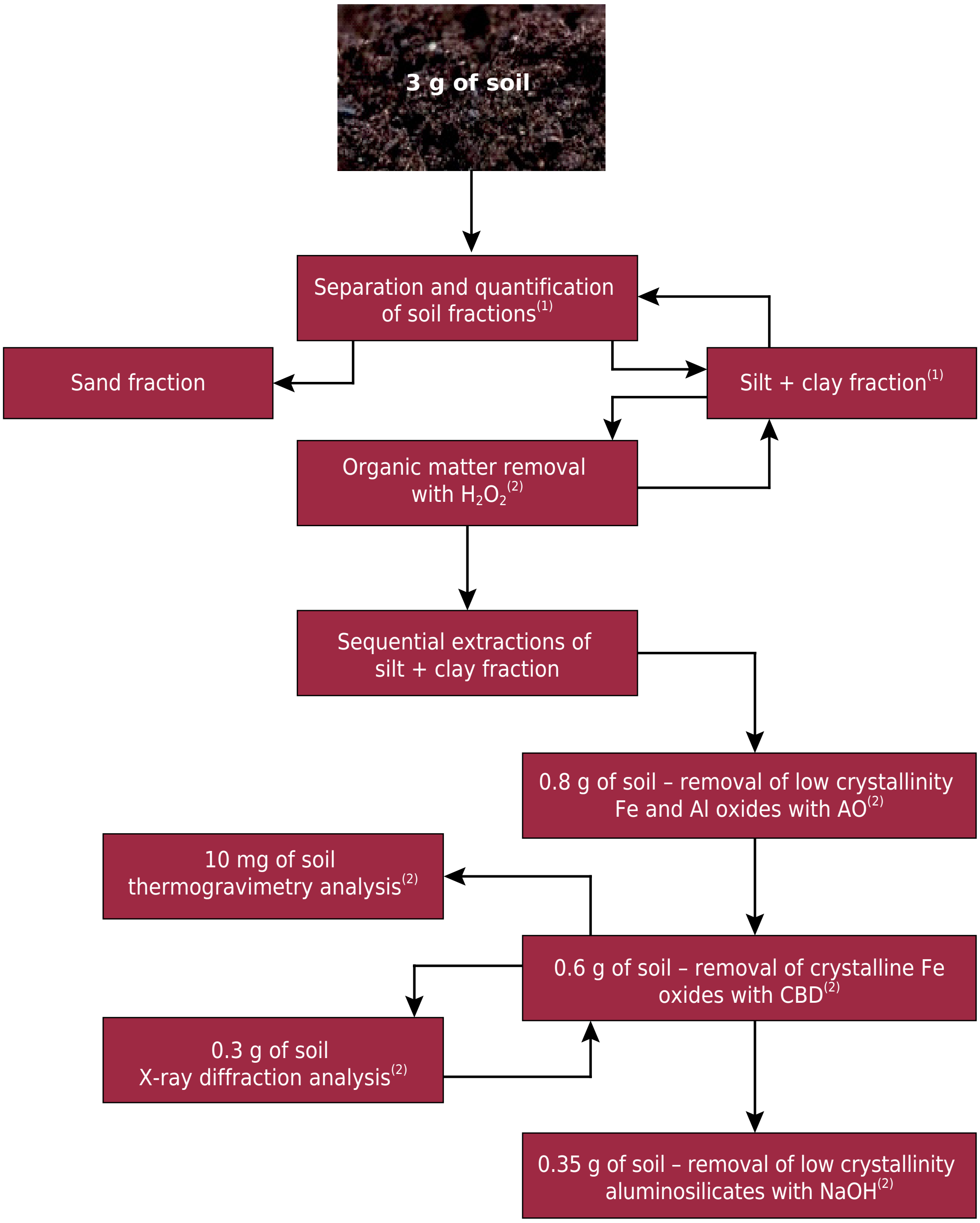

Figure 3. Scheme of analyses. Note: (1) non-destructive and (2) destructive analyses. H_2O_2: hydrogen peroxide; AO: ammonium oxalate; DCB: dithionite-citrate-bicarbonate; NaOH: sodium hydroxide.

Table 2. Iron and aluminum oxide contents and elements extracted by ammonium oxalate (AO) in the sequential treatments of the clay + silt fraction

Sample	Fe_2O_3	Al_2O_3	As	Ba	Ca	Cd	Cr	Cu	K	Mg	Mn	Ni	P	Pb	S	Si	V	Zn
	g kg^{-1}		mg kg^{-1}															
Site 1																		
1	14.0	14.8	4.5	26.1	41.8	0.2	16.8	17.1	401.5	574.8	150.3	2.2	577.2	13.9	669.2	715.3	19.7	34.7
2	15.2	17.1	4.1	24.5	55.1	0.3	18.6	11.4	343.1	358.5	196.8	2.1	534.4	13.8	661.5	760.7	22.3	29.1
3	13.8	11.6	3.4	30.7	45.9	0.2	10.7	10.1	277.0	500.7	135.3	1.7	532.0	12.0	471.2	627.5	19.1	26.0
4	12.1	10.1	3.2	25.1	35.9	0.2	9.1	8.8	293.5	422.8	98.8	1.7	510.6	30.1	411.9	552.8	17.9	21.2
5	12.6	12.6	3.7	43.2	31.2	0.2	13.4	10.8	423.9	753.7	250.6	1.8	584.7	23.7	620.3	579.2	18.8	27.9
6	13.0	13.8	3.8	48.2	31.5	0.2	16.5	10.8	657.9	951.0	252.8	2.1	572.3	14.5	695.5	605.5	18.4	29.1
7	12.8	13.3	2.7	51.1	32.5	0.2	14.8	9.4	490.1	837.2	273.3	2.2	680.5	11.0	744.0	571.1	18.0	22.2
Site 2																		
8	6.7	10.2	3.8	24.4	45.0	0.1	7.6	17.6	499.3	1632.3	168.8	1.2	527.0	20.8	560.3	550.9	8.7	17.2
9	8.8	9.0	4.3	93.7	31.3	0.2	16.0	21.1	2022.7	2242.0	359.6	4.9	1376.2	17.5	1191.2	651.3	18.7	89.0
10	6.6	10.4	2.8	31.4	34.5	0.1	7.9	14.1	528.2	1584.4	200.9	1.4	525.3	20.5	578.6	618.4	9.8	12.7
11	8.6	6.1	2.8	11.6	32.5	0.1	4.5	11.4	329.7	705.1	132.2	1.5	374.3	30.6	339.8	482.4	21.8	23.4
12	6.9	10.1	1.3	26.4	32.6	0.2	8.1	11.5	521.6	1602.2	187.8	2.4	452.4	21.2	544.8	409.4	9.0	33.5
13	5.9	9.6	2.2	26.9	37.3	0.1	6.8	14.3	410.0	1437.0	178.2	1.8	378.8	28.6	499.7	544.2	8.4	15.5
14	6.1	10.0	2.9	26.5	32.5	0.1	8.3	11.0	442.5	1693.8	191.7	1.4	411.4	26.5	623.6	577.7	9.0	18.6
Site 3																		
15	6.8	11.4	1.8	13.4	29.1	0.1	8.4	13.6	374.7	1160.1	87.5	1.1	302.0	10.1	296.5	416.0	16.3	24.9
16	6.1	10.1	1.6	23.3	27.7	0.1	7.2	14.4	342.3	1113.1	150.5	1.1	357.2	30.1	432.4	520.5	8.6	13.4
17	19.0	9.1	3.1	2.1	31.3	0.3	15.3	11.4	189.0	248.0	71.4	3.9	571.7	73.8	480.1	818.3	30.9	68.9
18	6.8	12.2	3.0	11.2	32.7	0.1	13.2	15.5	412.4	1845.4	90.4	1.0	285.5	7.8	401.9	583.9	17.7	14.3
19	6.6	11.2	3.0	10.9	32.2	0.1	8.2	10.9	398.2	1377.9	97.4	1.1	315.0	13.1	298.0	510.5	15.5	19.2
20	5.7	10.0	2.0	12.5	32.4	0.1	9.3	11.3	443.4	1545.8	100.3	1.6	299.1	26.2	340.4	507.3	14.2	16.2
21	6.3	11.1	3.2	13.0	33.4	0.1	10.3	14.7	449.4	1722.9	107.9	1.2	320.7	16.1	348.0	555.0	16.7	19.0
Site 4																		
22	7.7	12.6	3.3	8.1	37.7	0.1	8.6	12.1	256.9	485.6	80.2	1.3	350.0	10.7	537.9	426.7	18.8	25.6
23	17.1	12.2	3.0	65.3	47.9	0.3	16.8	32.0	850.5	3240.5	178.2	9.3	1196.5	3.4	833.1	808.7	19.8	178.5
24	21.9	10.7	3.6	73.8	38.9	0.3	16.1	26.1	875.1	2347.8	267.8	8.3	2012.1	10.7	1348.7	1001.7	33.7	152.3
25	24.5	8.8	3.7	26.0	39.7	0.4	14.2	19.0	505.0	773.6	156.0	4.7	1677.8	20.5	682.3	1036.1	24.5	86.4
26	10.7	8.0	2.8	146.2	67.3	0.2	8.9	23.1	1065.3	2990.4	362.7	4.6	2154.8	7.9	1282.7	623.4	19.0	109.2
27	11.3	10.0	3.4	89.5	42.0	0.2	16.3	32.5	938.7	3052.9	382.8	5.5	1792.4	24.1	2297.6	678.7	19.0	116.5
28	9.1	7.5	2.5	0.0	48.1	0.1	4.2	28.6	608.1	1772.2	345.9	2.7	2432.8	2.5	679.6	605.5	13.6	119.7
Samples collected by Federal Police																		
29	14.7	15.7	3.9	33.6	37.9	0.2	17.4	13.6	355.3	618.9	184.6	2.0	581.7	10.9	656.0	683.9	23.3	26.1
30	10.7	17.2	1.9	5.9	38.3	0.1	15.1	14.4	298.3	702.7	85.6	4.0	354.4	22.5	431.6	521.3	24.4	96.4
31	6.1	9.9	1.8	24.6	30.9	0.1	7.8	11.3	480.8	1582.5	186.1	1.5	389.7	18.9	572.2	548.2	8.7	13.5
32	9.7	9.4	2.9	111.4	34.0	0.1	17.3	20.5	2405.6	2465.4	397.5	4.8	1424.3	14.1	1343.6	595.1	18.8	82.4
33	18.7	21.1	4.4	31.5	38.7	0.4	24.9	11.7	423.8	507.5	268.6	2.7	567.7	8.6	820.7	882.1	29.7	31.3
34	7.3	13.2	2.4	11.4	31.0	0.1	15.4	10.2	520.2	1692.0	89.0	1.1	292.3	13.9	428.0	424.8	17.9	18.6
35	11.0	9.8	3.2	80.3	33.4	0.2	13.3	14.1	1141.9	1430.6	353.4	2.3	1032.9	20.8	773.5	673.0	18.4	38.5
36	14.7	16.6	3.9	37.1	34.7	0.2	20.2	12.4	389.2	835.2	210.1	2.4	544.9	5.0	774.9	707.0	22.5	27.9
37	6.8	12.5	3.2	11.7	34.7	0.1	15.6	12.2	519.9	2009.4	102.3	1.4	292.6	9.6	497.6	572.8	17.8	17.0
38	6.9	10.6	1.9	27.0	37.2	0.1	8.0	15.9	474.8	1562.6	184.2	1.4	390.6	12.9	561.2	575.3	10.2	16.4
39	11.0	10.1	3.0	95.7	36.4	0.2	14.4	17.9	1364.6	3271.8	329.7	3.4	1482.1	10.3	1365.8	626.8	19.7	77.7
40	14.8	18.0	3.8	28.4	40.2	0.2	22.9	12.8	386.7	688.8	110.0	2.4	512.2	8.0	854.0	721.9	20.8	30.1
41	7.1	12.4	2.5	11.0	37.5	0.1	14.9	11.4	514.5	1908.7	101.2	1.3	287.1	9.6	478.4	576.4	18.5	19.1

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Continuation

42	7.9	12.1	3.5	29.8	44.3	0.1	10.4	12.2	538.7	1906.9	214.0	1.4	412.5	17.1	673.7	676.3	11.4	15.0
43	12.5	14.5	3.5	47.8	33.2	0.2	16.7	12.6	495.5	732.0	308.6	2.0	672.0	15.6	855.2	729.8	17.4	24.6
44	7.3	12.2	2.2	12.6	34.8	0.0	14.1	8.5	460.2	1924.2	111.2	1.3	293.0	11.0	432.7	592.4	18.6	28.4
45	7.9	11.1	3.3	33.0	32.8	0.1	8.6	14.1	486.0	1826.0	203.4	1.4	481.4	11.8	603.1	688.3	11.6	21.4
46	11.4	10.0	4.2	112.5	46.2	0.2	13.8	21.1	1103.4	2546.2	368.8	4.0	1734.5	8.4	1443.6	656.3	21.4	77.1
47	7.3	13.2	2.1	10.3	39.1	0.1	15.9	12.0	557.8	1971.9	99.5	1.1	300.4	10.5	473.1	570.1	19.7	28.3
48	7.0	10.0	2.9	27.3	34.4	0.1	8.7	12.4	403.0	1721.1	185.9	1.3	551.3	9.5	671.9	580.8	9.6	13.3
49	12.9	11.6	4.0	32.5	34.8	0.2	9.5	9.3	399.7	576.5	197.4	1.7	670.1	12.0	423.0	654.1	18.4	20.5
50	6.6	11.2	1.9	13.3	32.8	0.1	11.5	9.4	406.0	1791.8	92.3	1.2	257.3	11.3	374.1	654.5	17.6	13.5
51	6.9	10.9	2.6	20.9	32.2	0.1	8.7	11.2	339.7	981.7	148.7	1.3	323.0	15.9	469.6	514.7	9.4	14.4
52	10.0	8.0	2.1	155.6	34.3	0.1	10.2	22.4	1158.6	2952.5	350.0	4.0	3837.4	2.1	1508.2	535.0	17.0	117.3

Extraction was performed with ammonium oxalate 0.2 mol L^{-1} at pH 3.0, in the dark (McKeague, 1978).

the mass loss due to the de-hydroxylation of these minerals when heated (Tan and Hajek, 1986).

Silt + clay mineralogical identification by X-ray diffraction (XRD)

Approximately 0.3 g of the silt + clay samples were prepared (random powder) for XRD analysis. The diffractograms were obtained by the equipment X' Pert[3] Powder, using a vertical goniometer and scanning from 3° to 60° 2θ at 1° 2θ min^{-1} in accelerator mode which presents a linear array of detectors adjusted to the fast mode, for 4 min and 48 s. The diffractometer is equipped with nickel filter and Cu Kα radiation and was operated at 20 mA and 40 kV.

Statistical analyses

All results were square root transformed and then analyzed using a principal component analysis (PCA) using the Statistica software (StatSoft, 2011) and Paleontological Statistics (PAST) software testing for Bray-Curtis similarities (Hammer et al., 2001). The similarity values were then used to link each sample to a specific location, and the accuracy of classification was reached by comparing the predicted sample location to the known true sample location.

The identification of the samples from the police was only revealed after all statistical analysis was completed, and the grouping of the samples collected by the researchers and experts was unknown.

RESULTS

Contents of low crystallinity Fe and Al oxides extracted by ammonium oxalate (AO) varied from 5.7 to 24.5 g kg^{-1} and 6.1 to 17.1 g kg^{-1}, respectively (Table 2). The higher contents of both oxides were related to the samples formed from claystone (i.e., sites 1 and 4), and the higher variation was observed for samples collected at site 4.

Contents of crystalline Fe_2O_3 (22.4 to 48.6 g kg^{-1}) extracted by dithionite-citrate-bicarbonate (DCB) were, approximately, the double in comparison to the AO extraction (5.7 to 24.5 g kg^{-1}) (Tables 2 and 3). In agreement with the lower contents of poor crystallinity Fe oxides verified in AO extracts, samples from site 2 and 3 showed higher contents of Fe_2O_3 extracted by DCB, ranging from 27.2 to 48.6 g kg^{-1}. As verified in the AO, the wide variation in the contents of Fe_2O_3-DCB and Al_2O_3-DCB belongs to the samples from site 4 (22.4 to 47 g kg^{-1} and 4.8 to 17.4 g kg^{-1}, respectively). Contents of Ca extracted by DCB (679.4 to 10,962.9 mg kg^{-1}) were much higher than the contents extracted by AO

Table 3. Iron and aluminum oxide contents and elements extracted by citrate-bicarbonate-dithionite (CBD) in the sequential treatments of the clay + silt fraction

Sample	Fe_2O_3	Al_2O_3	As	Ba	Ca	Cd	Cr	Cu	K	Mg	Mn	P	Pb	Si	V	Zn
	g kg^{-1}		mg kg^{-1}													
Site 1																
1	30.5	10.0	9.2	23.5	1080.5	0.4	9.8	1.1	938.4	77.1	67.8	949.5	14.9	2071.3	61.0	19.0
2	28.5	9.1	9.0	19.2	679.4	0.3	9.2	1.1	691.4	63.6	69.6	756.8	20.9	1837.0	58.9	15.9
3	29.9	9.3	9.7	25.3	1225.1	0.4	9.7	1.2	709.9	73.4	55.6	814.0	17.1	1861.9	62.2	16.2
4	28.4	8.9	8.3	20.4	884.6	0.3	9.3	0.6	669.8	57.0	48.7	783.0	30.3	1779.8	59.3	12.9
5	27.2	8.5	6.2	29.1	2304.3	0.3	9.2	0.9	683.6	74.8	107.4	801.9	21.3	1750.3	56.9	20.6
6	29.2	9.0	3.0	29.5	3035.0	0.3	9.5	1.3	694.7	74.0	106.0	819.9	19.5	1834.7	59.9	24.8
7	26.4	8.4	9.0	31.6	3483.5	0.3	9.4	0.7	671.2	70.9	121.2	841.6	22.9	1759.1	55.1	17.1
Site 2																
8	33.6	11.3	3.2	22.6	5357.9	0.5	8.6	0.5	746.4	101.5	118.1	930.7	14.8	1794.6	57.0	18.8
9	35.2	10.0	7.0	86.7	10962.9	0.6	19.9	1.3	1035.3	123.0	195.1	1295.6	18.7	2138.3	63.4	70.9
10	33.1	10.9	8.0	19.6	6139.7	0.5	8.4	0.4	776.4	103.3	150.3	968.7	12.1	1817.3	56.1	16.8
11	27.2	7.1	9.9	14.1	2508.9	0.4	6.3	0.8	688.9	72.3	61.6	805.8	20.5	2530.9	54.4	19.3
12	31.9	10.7	7.9	18.8	5733.0	0.5	8.5	1.0	830.5	99.6	134.1	925.5	67.8	1884.5	54.8	27.5
13	29.6	10.1	8.6	19.8	5080.6	0.4	7.6	0.5	745.6	96.8	119.7	874.6	16.7	1600.1	50.5	15.9
14	35.0	12.2	10.9	19.9	5677.9	0.6	9.6	1.3	777.2	121.9	140.4	967.2	18.3	1974.5	61.2	23.6
Site 3																
15	48.6	19.9	8.1	17.1	2534.3	0.6	19.4	0.5	801.3	119.7	60.0	1094.5	6.8	2055.6	118.4	26.9
16	35.6	11.5	6.9	18.3	2995.2	0.4	9.1	0.2	734.3	93.8	97.7	893.8	5.2	1712.5	62.8	17.2
17	35.6	9.8	9.5	6.5	269.3	0.4	12.7	0.4	746.1	73.1	32.8	891.5	20.7	2608.6	89.7	20.3
18	45.4	17.4	12.1	16.4	5682.4	0.6	18.0	0.7	769.8	143.5	62.1	974.8	8.7	1770.4	98.8	16.2
19	45.7	17.7	9.6	15.6	4886.8	0.6	17.9	0.8	801.5	123.4	59.4	1046.9	11.8	1938.7	102.1	19.5
20	42.1	16.1	5.3	15.2	4830.4	0.5	16.6	0.8	743.7	124.5	61.9	992.5	13.0	1734.5	94.0	18.0
21	47.8	18.3	14.8	20.1	6400.4	0.6	19.0	0.2	829.2	136.9	76.8	1110.4	13.4	1944.6	105.4	20.4
Site 4																
22	47.0	17.4	10.1	14.0	821.7	0.6	17.7	0.6	751.4	78.9	48.2	1014.5	8.6	1877.4	108.0	19.3
23	33.0	8.0	8.5	75.4	9183.6	0.5	12.3	0.7	841.1	154.8	141.6	1082.2	43.8	2608.2	61.6	103.4
24	24.6	4.8	6.4	60.4	8386.9	0.4	9.8	4.9	741.7	120.3	140.7	1008.8	48.0	2478.0	45.5	64.3
25	37.8	6.6	9.4	28.4	2887.6	0.4	14.6	1.3	731.4	78.2	83.7	1021.7	75.7	3152.3	73.9	36.6
26	25.2	5.9	8.7	107.8	10427.5	0.4	10.3	0.9	769.2	124.3	156.4	1165.8	18.8	1658.5	42.0	51.5
27	29.5	6.3	6.0	145.0	9103.1	0.6	11.6	1.5	849.8	239.1	248.7	1128.4	115.0	2000.8	44.6	77.2
28	22.4	5.2	6.1	207.1	9143.5	0.4	10.8	0.5	716.0	103.7	146.1	1135.8	8.4	1314.6	38.6	55.5
Samples collected by Federal Police																
29	30.3	9.6	9.8	25.3	1635.2	0.3	9.8	0.5	715.8	79.3	80.4	814.5	27.2	1856.4	62.6	16.7
30	48.2	17.3	9.4	14.0	946.1	0.6	18.0	1.3	744.8	90.0	54.5	1007.2	34.1	2139.0	107.4	30.3
31	35.2	11.6	4.7	20.5	5420.2	0.6	9.2	0.6	806.2	109.1	143.4	971.7	12.8	1924.6	59.6	19.4
32	39.4	10.5	8.8	74.8	12290.3	0.7	20.1	1.0	1110.9	145.9	229.9	1388.6	19.8	2385.6	70.4	67.8
33	25.5	8.5	6.3	22.0	1137.2	0.3	8.8	0.6	711.2	69.7	96.5	722.8	18.7	1816.3	53.5	17.8
34	48.6	18.6	9.9	18.5	2513.1	0.7	18.7	0.4	752.1	133.5	56.9	1014.6	6.3	1807.1	110.0	27.6
35	39.5	10.7	14.0	55.9	10301.7	0.6	18.7	1.2	881.6	115.0	216.8	1223.6	18.4	2326.2	74.7	50.1
36	29.1	9.0	9.9	26.4	2561.3	0.4	9.9	1.4	668.0	84.9	109.2	804.4	21.1	1849.0	60.5	20.1
37	48.8	18.9	8.3	15.7	4767.1	0.5	18.8	0.6	807.0	163.6	66.8	1062.6	6.8	1969.3	109.4	20.4
38	37.5	12.6	6.3	20.7	5941.2	0.5	9.8	0.7	761.5	119.3	137.6	975.8	14.7	2016.7	65.6	22.4
39	29.8	7.4	6.8	65.5	9884.1	0.5	10.8	1.2	830.9	190.7	184.2	1124.4	21.9	1905.7	53.2	50.7
40	32.3	10.5	10.0	25.2	1841.2	0.4	11.1	0.5	779.7	79.8	60.3	874.9	15.9	2011.9	67.5	21.6
41	47.0	18.2	10.3	15.7	4669.0	0.6	18.2	0.7	727.8	145.9	63.3	1016.3	10.3	1980.8	106.1	19.9

Continue

Continuation

42	34.7	11.2	8.3	21.2	5270.9	0.5	9.0	1.0	743.6	113.3	143.9	890.0	15.4	1915.4	59.2	17.7
43	31.5	9.9	4.3	30.3	3081.8	0.5	10.9	0.7	726.9	87.2	137.9	960.9	17.7	2050.2	63.5	20.1
44	48.7	18.8	12.8	17.3	5123.6	0.5	18.6	0.6	800.9	155.2	72.7	1072.0	4.9	2015.8	108.3	25.1
45	38.0	12.8	9.7	25.9	8331.9	0.6	10.0	0.9	862.2	123.5	177.2	1028.0	17.3	2236.0	65.3	37.5
46	36.8	8.6	3.4	95.1	12470.6	0.6	14.4	1.2	987.7	126.1	228.5	1427.9	19.7	2195.0	65.7	66.8
47	48.9	19.4	14.2	16.5	4916.5	0.6	19.5	0.6	783.8	159.6	65.0	1068.8	9.6	1921.4	112.7	24.2
48	35.9	12.6	6.0	22.1	6847.2	0.6	9.6	0.7	768.5	130.2	137.5	1030.2	13.6	1861.9	62.8	21.6
49	34.0	10.8	4.4	28.2	1691.6	0.5	11.5	1.2	772.3	72.7	94.3	977.5	12.9	2055.5	67.8	21.2
50	50.6	20.3	5.5	18.5	6394.2	0.7	20.8	0.7	928.9	175.0	68.8	1177.4	8.7	2004.6	116.7	22.8
51	45.4	15.6	10.8	23.9	3330.9	0.6	12.1	0.7	993.3	107.7	110.5	1151.2	11.6	2387.2	83.5	23.1
52	24.6	5.8	4.7	91.0	10249.9	0.4	11.5	0.4	835.8	138.4	161.4	1267.1	13.2	1633.7	42.2	49.6

DCB: three extractions with 9.6 mL of a solution of sodium citrate 0.3 mol L^{-1} + 1.2 mL of a solution of sodium bicarbonate 1.0 mol L^{-1} + 0.24 g of sodium dithionite (Mehra and Jackson, 1960).

(27.7 to 45.9 mg kg^{-1}). The higher values were observed in the samples from site 2 and 3, formed by a calcium-rich bedrock.

The Fe extraction boiling NaOH 0.5 mol L^{-1} was very limited (Table 4). The variations in the Al_2O_3 and SiO_2 contents in the frame of site 4 was expressive (Al_2O_3: 0.7 to 12.5 g kg^{-1} and SiO_2: 0.5 to 10 g kg^{-1}). The NaOH method was efficient in K extraction, which can clearly observed by the taller values of K-NaOH in relation to the other elements expressed by mg kg^{-1} (Table 4). Small and poorly crystalline illite layers must be extracted. The NaOH solution has very limited performance in the extraction of 2:1 aluminosilicates minerals (Melo et al., 2002). However, it is possible that exfoliated layers [very reduced mean crystal diameter - MCD (001)] and poorly crystallized illite can be extracted. The amount of 2:1 layers stacked in the direction *c* in the aluminosilicate minerals is quite variable. The process of exfoliation reduces the particle size of illite, which favors the solubilization in basic solutions (van Breemen and Buurman, 2002).

The analyses of silt + clay samples generated 48 chemical variables (Tables 2, 3, and 4) and the Principal Component Analysis (PCA) showed the first three principal components of the dataset variance accounted for 59.5 % of the variance (Figure 4). The contents of kaolinite and gibbsite by thermogravimetry analysis and identification of the mineralogical profile by XRD were removed from the data matrix due to their lowest discriminatory power among the all studied variables. The combination of the chemical variables obtained in the sequential extractions with AO, DCB, and NaOH in a 3D-PCA matrix considerably distributed the 52 samples according to their sites, even with the dispersion of the samples from site 4.

The grouping and dispersion of the samples are more visible in the analysis by Bray-Curtis clustering (Figure 5). The intragroup similarities were: blue - 94.5 %, blue without sample 1 - 96.4 %; green - 97.3 %; red - 96.9 %; purple - 93.0 %; combination of green + red - 95.1 %; combination of (green + red) + blue - 93.0 %; combination of (green + red + blue) + purple - 90.5 %. These results show that the group with the highest similarity was composed of soil samples collected in the neighborhood of Guarani in Colombo (green). On the other hand, samples collected in the Boa Vista neighborhood in Curitiba (purple) had the lowest similarities. The set of all the samples presented similarity of 90.5 %. Some samples have dispersed from their original groups: sample 11 (green) grouped with blue; samples 17 (red) and 25 (purple) grouped in a isolate group; samples 16 and 51 (red) grouped with green; samples 22 and 30 (purple) grouped with red; sample 9 (green) grouped with purple. The total percentage of samples positioned outside their original groups was 15.4 %.

Table 4. Iron, aluminium, and silicon oxide contents and elements extracted by NaOH 0.5 mol L^{-1} in the sequential treatments of the clay + silt fraction

Sample	Fe_2O_3	SiO_2	Al_2O_3	Ba	Cr	Cu	K	Mg	Mn	Mo	P	S	V	Zn
	g kg^{-1}			mg kg^{-1}										
Site 1														
1	0.1	6.2	9.1	0.3	0.4	11.1	133.1	0.8	0.5	0.9	69.9	76.4	1.0	2.7
2	0.1	7.0	8.4	0.1	0.4	13.7	126.7	0.6	0.6	1.0	66.0	70.1	1.2	2.4
3	0.1	6.7	7.9	0.1	0.4	16.0	169.8	0.6	0.5	0.8	60.6	77.7	1.1	3.2
4	0.1	6.4	7.3	0.1	0.4	14.9	139.0	0.6	0.4	1.2	68.4	90.6	1.1	2.0
5	0.1	7.0	8.2	0.1	0.4	15.8	140.6	0.5	0.6	0.6	75.1	97.0	1.2	1.9
6	0.1	7.0	8.5	0.1	0.5	14.0	133.6	0.7	0.8	1.0	66.8	77.5	1.1	2.2
7	0.1	7.0	7.9	0.1	0.5	20.3	160.4	0.9	1.0	0.8	69.3	98.7	1.1	2.7
Site 2														
8	0.0	6.4	9.3	0.1	0.5	9.6	169.1	0.7	0.6	0.7	87.8	63.8	1.1	3.3
9	0.1	5.3	10.0	0.2	0.6	8.1	203.9	0.5	0.5	0.9	120.0	92.7	1.6	6.1
10	0.1	6.6	9.7	0.2	0.4	5.6	175.3	0.6	0.8	0.5	85.3	62.2	1.1	2.8
11	0.1	17.1	6.2	0.1	0.3	15.8	148.9	0.5	0.6	0.9	49.9	123.0	1.5	1.6
12	0.1	5.9	8.5	0.1	0.4	10.7	169.8	0.5	0.6	1.1	73.9	70.9	1.0	3.7
13	0.0	6.4	9.3	0.1	0.4	6.6	173.6	0.6	0.5	0.7	69.9	60.9	0.9	3.4
14	0.0	6.2	9.3	0.1	0.4	7.2	169.2	0.5	0.6	0.7	75.0	63.7	1.0	2.3
Site 3														
15	0.0	4.0	11.3	0.1	0.5	9.7	149.6	0.5	0.2	0.6	95.8	75.8	2.3	4.8
16	0.0	5.8	8.5	0.1	0.4	6.0	152.6	0.6	0.4	0.7	86.6	67.2	1.1	2.1
17	0.0	10.1	6.5	0.1	0.4	6.9	172.6	0.6	0.2	0.6	53.7	67.5	2.1	1.7
18	0.1	7.9	5.5	0.1	0.5	15.1	154.9	0.5	0.4	0.6	74.4	93.1	1.6	5.2
19	0.0	4.9	13.9	0.1	0.5	6.4	171.3	0.8	0.2	0.6	97.3	79.5	2.8	1.7
20	0.0	4.3	12.1	0.1	0.5	5.9	176.1	0.6	0.2	0.8	99.2	81.1	2.7	2.1
21	0.0	4.7	13.7	0.1	0.5	6.5	167.0	0.4	0.2	0.9	120.4	72.8	3.2	2.7
Site 4														
22	0.1	4.4	12.5	0.0	0.5	7.5	164.8	0.5	0.2	0.8	103.0	81.6	2.6	3.2
23	0.0	0.5	0.7	0.1	0.2	0.9	177.4	0.4	0.1	0.8	8.5	16.9	0.2	0.6
24	0.1	9.0	3.8	0.0	0.4	18.1	174.5	0.7	0.9	0.6	45.4	107.5	0.9	5.1
25	0.1	10.0	5.0	0.1	0.4	16.9	154.2	1.3	0.8	0.5	41.2	85.7	1.0	60.9
26	0.0	1.9	2.6	0.3	0.4	10.6	181.2	0.9	0.2	0.5	18.0	170.3	0.4	6.6
27	0.0	2.1	3.0	0.3	0.3	14.2	190.4	0.7	0.1	0.7	13.8	97.5	0.3	27.7
28	0.0	1.6	2.4	0.4	0.4	11.2	163.0	0.8	0.1	0.5	20.7	79.5	0.4	7.5
Samples collected by Federal Police														
29	0.1	6.9	8.2	0.0	0.6	13.1	150.9	0.7	0.7	0.5	78.3	81.9	1.1	6.0
30	0.0	4.3	10.7	0.1	0.4	6.7	139.6	0.6	0.2	0.6	86.2	83.3	2.5	2.7
31	0.1	5.9	8.7	0.1	0.4	9.5	164.9	0.7	0.6	0.7	77.2	66.6	1.1	7.1
32	0.1	5.2	10.1	0.1	0.8	11.5	207.3	0.7	0.9	0.7	127.1	110.3	1.7	15.1
33	0.1	7.5	8.7	0.0	0.6	13.8	146.1	0.7	0.8	0.6	92.8	117.6	1.3	3.6
34	0.0	3.9	12.2	0.0	0.5	6.5	146.9	0.5	0.2	0.6	121.3	88.0	3.1	22.9
35	0.1	5.5	9.4	0.1	0.6	13.3	162.4	0.9	0.8	0.5	105.2	75.3	1.2	4.9
36	0.1	6.6	7.8	0.1	0.5	16.7	162.7	0.8	0.6	0.5	79.8	110.8	1.4	2.5
37	0.0	4.3	12.9	0.0	0.4	6.1	156.6	0.6	0.2	0.7	121.3	82.4	3.1	6.3
38	0.1	5.7	8.4	0.0	0.5	11.6	152.9	0.7	0.5	1.2	92.0	100.1	0.9	3.2
39	0.0	4.2	4.8	0.1	0.3	11.3	170.8	0.9	0.3	0.9	55.6	80.4	0.4	5.1
40	0.1	5.0	6.0	0.0	0.4	13.1	99.2	0.7	0.4	0.4	53.9	75.5	0.8	2.1

Continue

Continuation

41	0.0	4.4	13.4	0.0	0.4	7.1	168.0	0.4	0.2	0.6	106.0	96.2	2.8	2.1
42	0.1	6.2	9.3	0.1	0.5	6.9	167.3	0.5	0.7	0.6	77.4	73.7	1.2	3.9
43	0.1	6.2	7.3	0.1	0.5	17.9	172.3	0.6	1.2	0.8	85.3	121.1	1.2	4.0
44	0.0	4.6	13.2	0.1	0.5	7.0	158.6	0.6	0.2	0.6	105.4	83.7	2.7	9.0
45	0.1	6.6	9.6	0.0	0.5	8.8	184.2	0.4	0.7	0.4	90.7	85.1	1.0	3.4
46	0.0	4.2	4.4	0.1	0.5	10.0	183.8	0.6	0.4	0.8	72.1	73.9	0.7	3.6
47	0.0	4.5	13.7	0.1	0.5	6.0	172.6	0.4	0.2	0.8	109.4	71.2	2.9	3.3
48	0.1	5.6	8.7	0.1	0.4	8.6	180.9	0.8	0.6	1.0	83.2	85.9	1.2	3.9
49	0.1	6.6	8.1	0.1	0.6	16.8	148.3	0.5	0.7	0.6	92.0	133.0	1.2	6.0
50	0.0	4.1	12.9	0.1	0.5	7.2	175.2	0.4	0.1	0.5	109.3	79.1	2.9	6.2
51	0.0	5.7	9.2	0.1	0.3	7.7	168.0	0.5	0.4	0.5	81.3	79.8	1.0	2.7
52	0.0	1.7	2.5	0.3	0.3	8.1	208.9	0.6	0.2	0.8	16.1	82.3	0.4	2.9

NaOH: samples were disposed in tubes with cold 2 mL of NaOH 0.5 mol L^{-1}. After moisture, 15 mL of the NaOH 0.5 mol L^{-1} at 200 °C was added to the samples. The boiling solution remained in contact with the sample for three minutes. Immediately after, samples were cooled in a recipient with cool water (Jackson et al., 1986; Melo et al., 2002).

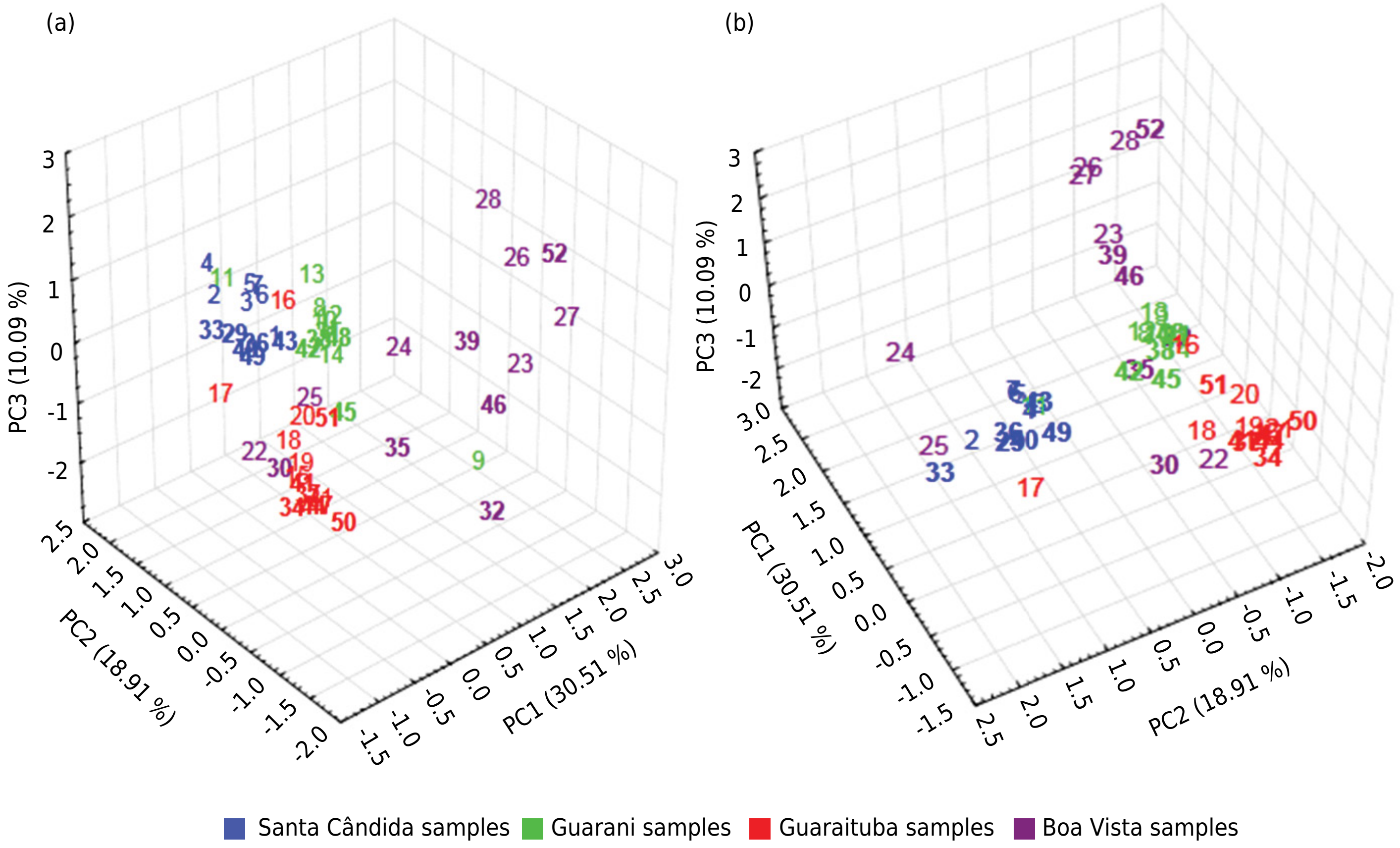

Figure 4. 3D-Principal Component Analysis (PCA) in two orientations a) and b), for all samples, distributed according the variables analysed. Blue-samples - Santa Candida; green-samples – Guarani; red-samples – Guaraituba; purple-samples - Boa Vista. Samples highlighted in dark colours were collected by Federal Police. Note: samples from 1 to 28 were collected by the researches from UFPR; samples from 29-52 were collected by the criminal expertises from Federal Police (Table 1).

DISCUSSION

Oxides extracted by AO are related to the poorly ordered Al and Fe minerals, which are widely reactive in soils due to their large specific surface area (Simas et al., 2006; Mendonça et al., 2013). Their formation and concentration are greatly influenced by environmental conditions, mainly in soils with elevated moisture and organic matter

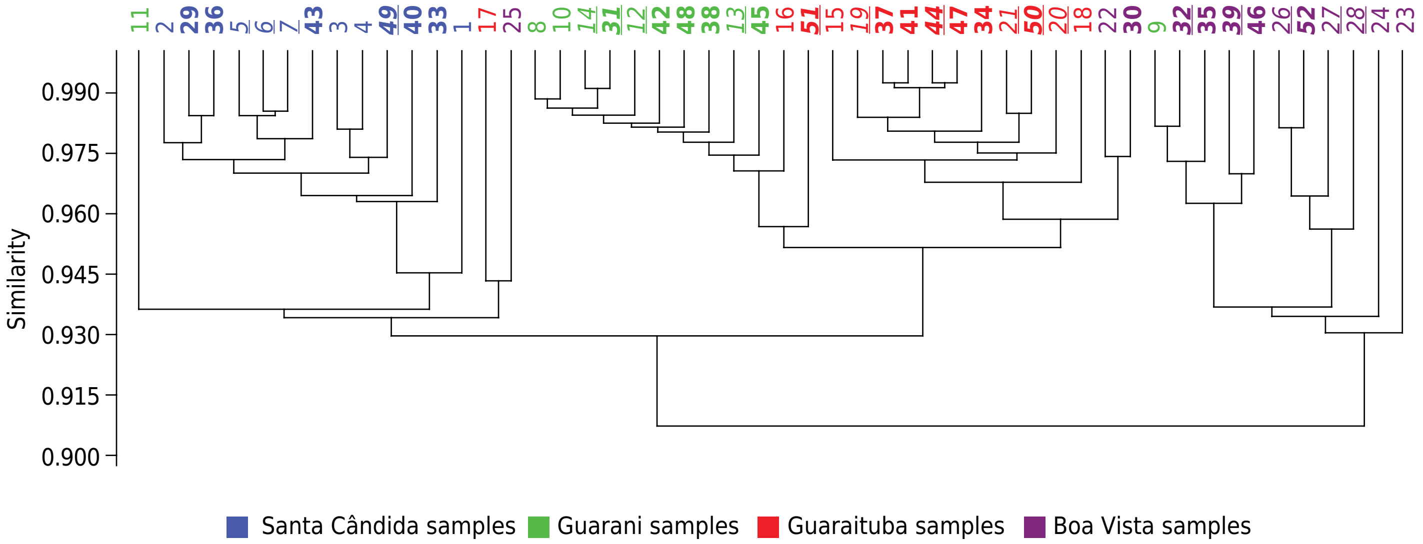

Figure 5. Diagram of Bray-Curtis similarity for all samples, distributed according the variables analysed. Colours: blue samples - Santa Candida; green samples – Guarani; red samples – Guaraituba; purple samples - Boa Vista. Samples highlighted in dark colours and in bigger font were collected by Federal Police. Note: Samples from 1 to 28 were collected by the researches from UFPR; samples from 29-52 were collected by the criminal expertises from Federal Police (Table 1).

and low pH (Melo et al., 2001). The low contents of Fe_2O_3-AO indicate that the crystalline form predominates in these soils. In most samples, the Al_2O_3-AO contents were higher than the Fe_2O_3-AO contents, attributed to the dissolution of Al gels (gibbsite precursors) by the AO (Ghidin et al., 2006; Melo et al., 2008).

The predominance of Fe crystalline oxides can be explained by weathering processes. The release of Al during the DCB extraction is due to the dissolution of goethite and hematite with isomorphic substitution of Fe by Al in the mineral structure due to similar ionic charge, ionic radius, and coordination of Al and Fe (Schwertmann and Kämpf, 1985; Schwertmann and Taylor, 1989).

Contents of Si and Al extracted by boiling NaOH 0.5 mol L^{-1} represent the poorly crystalline aluminosilicates (short-range order Al-hydroxide, Al-O-Si layers and Si-O-opaline silica) and gibbsite. The highest variations of Fe_2O_3, Al_2O_3, and SiO_2 extracted by AO, DCB, and NaOH for samples collected at site 4 might be due to a considerable deposition of artifacts and waste found in that location, being a largely heterogeneous environment.

Figure 5 shows a satisfactory grouping of the samples collected by the researchers and also by the police. The proximity of the trace samples, collected from the sole of the boot in the simulated crime scene, strongly demonstrates the good application of the SOP by the police, as well as their potential for calibration of sampling. There was dispersion of only one trace sample (sample 51), which could be related to the differences commonly found in the environmental conditions. Elemental chemical results showed the similarity between the samples from the same frame and the same footprint (vestige) and were clearly able to discriminate the samples intergroup according to different neighborhoods and different parent material selected in the study. Soils formed on different bedrocks were expected to discriminate from each other than soils developed on the same parent material. Therefore, soils from different geologies may be distinguished by a wide range of techniques (Dawson and Hillier, 2010), but few techniques can discriminate soils that are similar but not identical (Dawson and Mayes, 2015; Prandel et al., 2017; Corrêa et al., 2018).

Our protocol of analyses showed a high capacity to discriminate the samples among the four sites using 48 soil chemical variables obtained from 3.0 g of soil (Figures 4 and 5).

With smaller quantities of samples (around 1 g), it was also possible to apply the same protocol of analysis (Melo et al., 2008). The selected 48 variables generated from chemical analyses have shown a capacity to discriminate between samples. A similar forensic study conducted in southern Brazil on Inceptisols (*Cambissolos*) from five locations examined 56 variables on soil silt + clay and also concluded that a set composed of only 16 variables could more readily efficiently distinguish soil samples than the whole dataset (Melo et al., 2008). The 3D-PCA and the similarity analysis as well showed the potential of the SOP for soil sampling in forensic case works. A few grams of soil are usually available at crime scenes, although not from questioned samples.

CONCLUSIONS

Most of the samples were correctly grouped according to their location of origin at all four sites tested, showing the ability to use chemical characterization to test a link between a questioned sample and a crime scene. The researcher and the police sampling groups also found the same results, showing potential for successful use of the Standard Operating Procedure (SOP) in real crime scenes by police practitioners.

Besides the calibration of the present SOP and the potential of the sequential chemical extractions, we must consider specific conditions attributed to the analytical approach in each case work. Intense anthropic activities, such as domestic waste disposal in urban areas reduced the discrimination power of the tested chemical analytical protocol. As future considerations, modifications to the sample treatment and analytical protocol could be made depending on the context of the forensic work, always improving on the best methodologies for the forensic examination of soil samples.

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