

## **Mineralogical Characterization of Pozuzo District's Soils through Physical Techniques**

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### **Abstract**

We introduce a study on soils in three different fields of plantations in Pozuzo District, Oxapampa province, Peru. Two of the fields are cultivated and the third one has a degradation problem. In situ, in all, we collected 29 samples in the three plantations. We utilized analytical and physical techniques, namely, energy dispersive X-ray fluorescence, X-ray diffractometry, and transmission Mössbauer spectroscopy; we complemented our research with a physical-chemical analysis to determine texture, pH, content of organic matter and cation interchange capacity. For all analyzed samples, the results of the analysis by energy dispersive X-ray fluorescence show the presence of the following elements: Si, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr and Zr. By X-ray diffractometry, we observe the structural phases associated with quartz, montmorillonite, illite, microcline, kaolinite, muscovite, and iron oxides such as goethite and hematite. By using transmission Mössbauer spectroscopy, we observe the presence of magnetic sextets assigned to Fe<sup>3+</sup> from hematite (Fe<sub>2</sub>O<sub>3</sub>); doublets associated with Fe<sup>3+</sup> and Fe<sup>2+</sup>, respectively, localized in illite and/or interstratified montmorillonite; similarly, we observe other states attributed to a Fe<sup>3+</sup> site. The results of the physical-chemical analyses of the plantations are of great importance to determine the soil conditions. Furthermore, a low level of organic matter is observed with a pH ranging from 4.6 to 6.0, what limits the nutrient absorption by the plants.

**Keywords** : X-ray diffraction, X-ray fluorescence, Mössbauer spectroscopy, Iron oxides.

### **Introduction**

Nowadays, in Peru there are reports on soils of coffee plantations located in ten different regions, work made by the Ministry of Agriculture (Peru' Ministry of Agriculture 2003); however, information on the mineralogy of iron oxides is indeed scarce. By means of this paper, we present a study based on mineralogical characterization of iron oxides in both soils suitable for agriculture and soils having problems of degradation (Cerón Loayza 2001, Trujillo Quinde 2004, Bustos Rodríguez 2012, Acevedo-Sandoval 2004); the samples were obtained in situ from horizons B1 (approximately 10-35 cm) from three different plantations: (1) coffee plantation, (2) grazing land, and (3) Shapumba land (it is a plant that grows in degraded soils). They were obtained in Pozuzo District, located in Oxapampa province, Pasco region. Pozuzo covers an area of approximately 1 300 km<sup>2</sup> on the eastern slopes of the Peruvian Andes in the region called central rainforest (see

Figure 1). This district depends on stockbreeding, agriculture and tourism; their geographical coordinates are between 9°52'30" and 10°18'30" south latitude, and between 77°03'33" and 77°52'30" west longitude; the annual rainfall is 1 717.00 mm, the annual average temperature is 17.3°C. 14 of out 29 collected samples were selected for analysis; they were the most representative. We grouped and codified them as follows: (a) coffee plantation: M-68 and M-69; (b) grazing land: M-59, M-76, M-77, M-78, M-80, M-81, M-82, M-83, M-84, M-85 and M-86; (c) Shapumba land: M-79.



**Figure 1.** Location of Pozuzo District, Pasco Region, Republic of Peru.

## Materials and Experimental Procedures

We collected all the samples in situ; next, we proceeded to dry them in a muffle furnace at 27°C, to grind them in an agate mortar, and to sift them in stainless steel sieves of 2 mm and 38 µm in order to obtain <2 mm- and <38 µm- size fractions, sandy and silty, respectively. Then, they were analyzed by the physical techniques EDXRF, XRD and TMS. The results were complemented by physical-chemical analyses such as content of organic matter (COM); cation interchange capacity (CIC); element contents of Fe, Cu, Mn, Al, Zn and P (in ppm); acidity (pH) by using a pHTestr2, brand OAKTON. Likewise, it was done a mechanical analysis to obtain the texture and size fractions of the samples, as it is shown in Table 1. The results show a variety of percentages of clay which do not exceed 45%.

**Table 1.** Physical-chemical analysis of all selected samples (14)

Sample	pH	COM	CIC (ppm)	Mechanical Analysis			
				1:1	%	Sand (%)	Silt (%)
M-59	5.1	1.0	6.10	20.0	46.0	34.0	Silty clay loam
M-68	5.7	2.6	4.05	78.0	14.0	8.0	Loamy sand
M-69	6.0	2.2	6.86	48.0	34.0	18.0	Sandy clay loam
M-76	5.4	3.3	5.80	38.0	38.0	24.0	Loam
M-77	5.2	2.9	7.00	26.0	46.0	28.0	Clay loam
M-78	4.7	2.9	5.80	44.0	38.0	18.0	Loam
M-79	4.5	4.6	3.80	66.0	22.0	12.0	Sand loam
M-80	4.8	1.0	5.80	16.0	40.0	44.0	Silty clay
M-81	4.7	2.4	7.50	42.0	40.0	18.0	Loam
M-82	4.7	3.1	4.20	36.0	40.0	24.0	Loam
M-83	5.1	2.6	4.90	24.0	60.0	16.0	Silt loam
M-84	5.4	3.9	7.50	26.0	60.0	14.0	Silt loam
M-85	4.7	2.0	6.20	44.0	32.0	24.0	Loam
M-86	4.0	2.6	4.60	26.0	40.0	34.0	Clay loam

*Analysis by Energy Dispersive X-Ray Fluorescence (EDXRF)*

An elemental composition analysis was performed by using a portable EDXRF of AMPTEK Inc., instrument that uses an X-ray tube with an Ag anode operating at 30 kV and about 30  $\mu$ A. This instrument allowed us the identification of elements with an atomic number greater than 12. We fitted the experimental EDXRF spectrum by utilizing an EDXRF spectra simulator, which is based on a fundamental-parameters model; the simulator program is written in FORTRAN language. Table 2 shows results of the quantitative analysis for some chosen samples; the uncertainty estimated in these measurements of elemental concentrations, is about 10%.

*Analysis by X-Ray Diffractometry (XRD)*

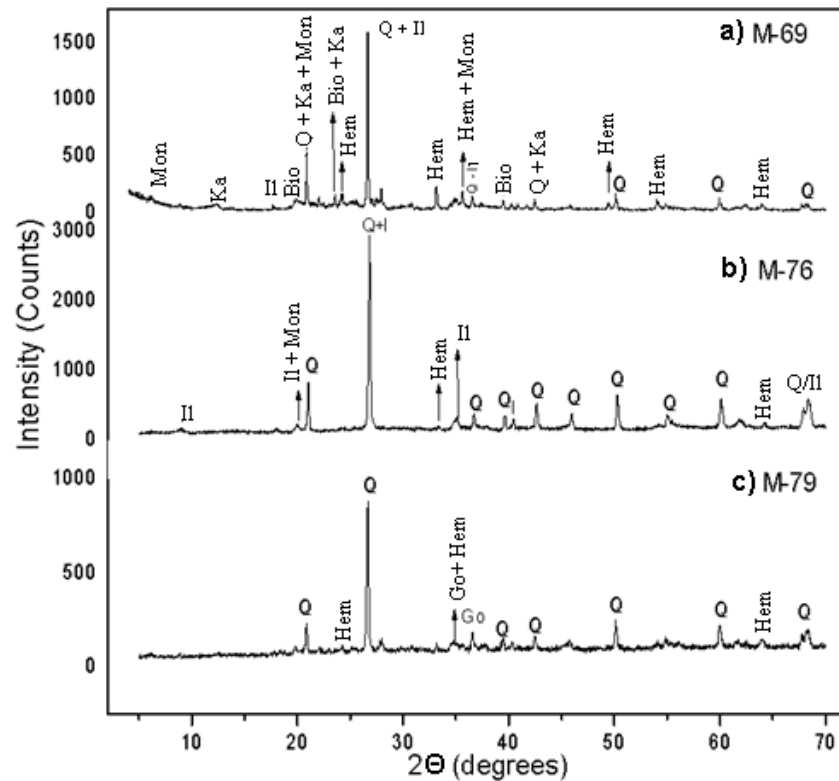
For structural analysis of the minerals existing in the samples, the XRD technique was applied by using a RIGAKU diffractometer, Miniflex model. We utilize the diffractometer in a configuration called Bragg-Brentano ( $\theta$ - $2\theta$ ). The X-ray generator has an X-ray tube, whose anode is made of copper that provides Cu-K $\alpha$  radiation with  $\lambda=1.54178$  Å; the tube output voltage is 30 kV, the tube output current is 15 mA. A NaI(Tl) scintillation detector was utilized for detection of X-rays. The goniometer is vertical, with 150 mm of radius; the scanned angle interval was  $4^\circ < 2\theta < 70^\circ$  and the  $2\theta$  advance was of  $0.02^\circ/\text{step}$  with a time interval of 2s/step.

**Table 2.** EDXRF quantitative analysis of 6 samples out of 14

Sample	Element (%)													
	Si	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr	Zr	La
M-76	40.4	0.24	2.28	0.18	0.41	0.01	0.10	2.95	0.01	0.01	0.02	0.01	0.02	0.02
M-77	41.9	0.18	1.50	0.18	0.46	0.01	0.23	3.16	0.01	0.02	0.01	0.004	0.01	0.03
M-78	46.5	0.23	2.00	0.14	0.51	0.01	0.16	2.87	0.01	0.03	0.02	0.01	0.03	0.03
M-79	20.1	0.10	0.91	0.26	0.32	0.01	0.06	3.19	0.01	0.01	0.01	0.00	0.01	0.03
M-80	34.8	0.21	1.98	0.16	0.48	0.01	0.10	3.43	0.001	0.01	0.01	0.00	0.02	0.04
M-81	35.9	0.21	1.65	0.14	0.38	0.02	0.11	2.76	0.001	0.03	0.01	0.00	0.02	0.04

*Analysis by  $^{57}\text{Fe}$  Transmission Mössbauer Spectroscopy (TMS)*

The TMS was utilized to obtain more detailed information about iron contained in the minerals. A conventional spectrometer was used with a signal of sinusoidal velocity modulation; with a multichannel analyzer (1024). Mössbauer spectrum for each measured sample at room temperature (RT) was obtained in the Laboratory of Soil Analysis and Archaeometry, Faculty of Physical Sciences, UNMSM; a  $^{57}\text{Co}$  source in an Rh matrix was utilized to get the spectra, which were analyzed by using Normos program written by R. Brand, Normos Site (Brand 1994); approximately 200 mg of powder sample were used to obtain an optimum thickness.



**Figure 2.** Diffractograms of a) sample M-69, from coffee plantations, showing Montmorillonite (Mon), Kaolinite (Ka), Illite (Il), Quartz (Q), Biotite (Bio), and Hematite (Hem); b) sample M-76 from pasture plantations showing Mon, Il, Q, and Hem; c) sample M-79, from *Shapumba* plantations, showing Q, Hem and Goethite (Go).

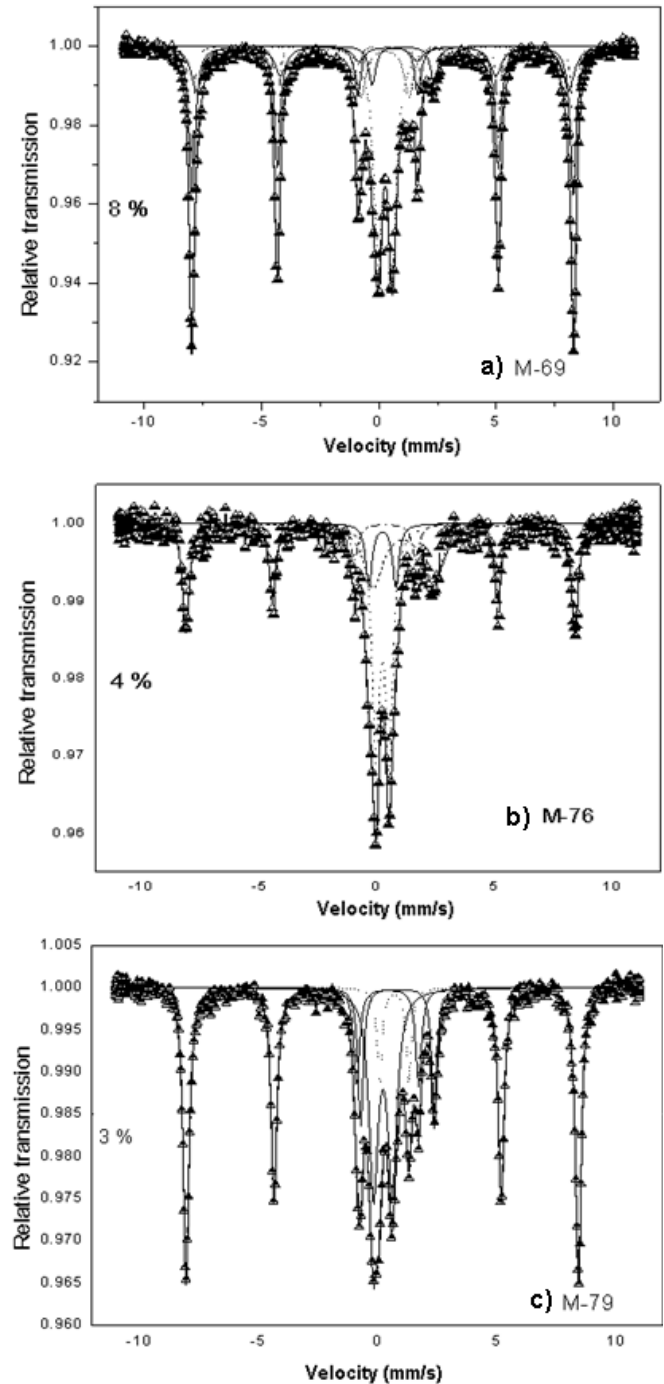
## Results and Discussion

By using EDXRF, in all analyzed samples (6 out of 14), we have identified the presence of the following micronutrients: Mn, Fe, Cu and Zn. Likewise, we find other elements such as Cl, K, Ca, Ti, Cr, Rb, Sr, Zr and La; it is displayed in Table 2. Therein, we realize that a greater concentration of Si, Fe and K exist in samples from grazing land; a lower percentage concentration in the *Shapumba* sample. In the case of Ca its concentration is slightly larger in *Shapumba* sample. In Figure 2, we observe results from XRD (Moore and Reynolds, Jr. 1997) for three representative samples (one for each plantation); so, we observe that the major peaks are due to the primary mineral, that is, quartz. In sample M-69, peaks overlapping is observed due to reflections from phyllosilicates and hematite (for interplanar distances of 0.366 nm and 0.269 nm) (Acebal 2000). However, in sample M-76 low intensities are observed for reflections from hematite; besides, those intensities are due to 2:1 type clay minerals such as interstratified illite-montmorillonite; furthermore, relatively strong reflections due to

kaolinite can be viewed. In sample M-79 we observed so peaks overlapping as reflection peaks broadening from reflective hematite and goethite - - at an interplanar distance of approximately 0.257 nm, with very poor crystallinity, what provokes an imprecise determination of their position.

On the other hand, three representative TMS spectra are displayed in the Figure 3: M-69 corresponding to coffee plantation; M-76, grazing land; and M-79, *Shapumba* land. Table 3 lists all hyperfine parameters required to fit the TMS spectra of the Figure 3 (Stevens 1998); in that table we observe the presence of the magnetic sextet S1 in all the samples except in M-83. Additionally, we notice sextets S2 and S3 in spectrum M-69 from coffee plantations; all three sextets were assigned to  $\text{Fe}^{3+}$  from hematite. The doublets are listed in nine groups, from D1 to D9, according to affinity for values of isomer shift and quadrupole splitting only. So, at least four doublets were required to fit the spectra of some samples. Doublet D4 is assigned to  $\text{Fe}^{3+}$  sites in kaolinite as observed in M-69. For grazing lands we note the presence of paramagnetic doublets D1 and D2, which are caused by  $\text{Fe}^{2+}$  cations located in illite and

montmorillonite; additionally; doublets from D3 to D9 are associated with  $\text{Fe}^{3+}$  sites. In M-83 we notice the presence of two paramagnetic doublets only, *i.e.* D4 and D5. In M-68 from coffee plantations, we observe an only sextet S1, but in M-69, also from coffee plantations, we notice sextets S1, S2 and S3. In M-69 we realize S1 has a hyperfine field  $B_{\text{hf}}=50.4$  T, and in M-68 we also see that S1 has a lower hyperfine field  $B_{\text{hf}}=49.2$  T, which correspond to weakly ferromagnetic hematite. This suggests us that in these samples an Al substitution for Fe happened, which causes a decrease in the magnetic field. In M-79, Shapumba plantation, from the XRD- and TMS- results, we have identified the presence of phases of goethite and hematite; doublet D5 is assigned to goethite in superparamagnetic state. The earlier sample has the highest COM with a low pH; therefore, we hypothesize that weathering and a high COM create favorable conditions for transformation from hematite into goethite.



**Figure 3.** Mössbauer spectra of the following samples: (a) M-69, coffee plantation, (b) M-76, grazing land, and (c) M-79, Shapumba land.

**Table 3.** Mössbauer parameters of nine samples from Pozuzo. ISO,  $2\varepsilon$ , QUA: mm/s; Bhf: T, and Area: %

Sample	Param	M-68	M-69	M-76	M-77	M-78	M-79	M-81	M-83	M-85
S1	ISO	0.19	0.23	0.21	0.18	0.22	0.30	0.27		0.28
	$2\varepsilon$	-0.22	-0.20	-0.25	-0.19	-0.19	-0.22	-0.21		-0.23
	Bhf	49.2	50.4	51.3	51.0	51.2	51.1	51.1		51.1
	Area	9	31	32	24	25	49	33		40
S2	ISO		0.22							
	$2\varepsilon$		-0.29							
	Bhf		50.6							
	Area		16							
S3	ISO		0.25							
	$2\varepsilon$		-0.23							
	Bhf		49.2							
	Area		16							
D1 (II/Bio) Fe <sup>2+</sup>	ISO	1.11	1.04	1.06	1.14	1.13		0.97		
	QUA	2.43	2.63	2.64	2.45	2.54		2.850		
	Area	42	4	25	12	12		10		
D2 (Mon) Fe <sup>2+</sup>	ISO	0.83	0.28				0.83			0.38
	QUA	2.54	2.04				3.09			2.35
	Area	10	7				10			7
D3 Fe <sup>3+</sup>	ISO						0.69			
	QUA						1.22			
	Area						7			
D4 Fe <sup>3+</sup>	ISO	0.21	0.27	0.20	0.20	0.21			0.26	0.25
	QUA	0.94	0.60	0.56	0.60	0.63			0.66	0.77
	Area	19	27	35	27	47			61	30
D5 Fe <sup>3+</sup>	ISO						0.22	0.29	0.23	
	QUA						0.81	0.83	0.88	
	Area						25	46	39	
D6 Fe <sup>3+</sup>	ISO									0.25
	QUA									0.45
	Area									21
D7 Fe <sup>3+</sup>	ISO	0.46								0.62
	QUA	0.78								0.95
	Area	21								3
D8 Fe <sup>3+</sup>	ISO			0.19	0.18	0.15		0.25		
	QUA			1.16	0.81	1.08		1.37		
	Area			8	38	17		11		
D9 Fe <sup>3+</sup>	ISO						0.62			
	QUA						1.50			
	Area						9			

The results of the physical-chemical analysis of the plantations are important to determine the soil conditions; the soil from grazing land is associated with a low level of COM, from 2 to 5; and, with a low pH in the range from 4.7 to 5.4. These two last facts limit the nutrients absorption by the plants. The soil from coffee plantations present a low COM between 2.2 and 2.6, and a mildly acid pH, from 5.7 to 6.0, less acid than in the grazing land samples. *Shapumba* soils have a pH of 4.5, which indicates a strongly acid soil, and a COM of 4.6, which is high compared with other samples. The reduction of COM causes effects on the soil productivity, and decreases CIC; pH tends to increase because COM tends to acidify the soil, what could be happening to M-79, the *Shapumba* sample.

## Conclusions

By using several analytical techniques we have carried out a research on the elemental and mineralogical characterization of field soils, with contrasting properties, such as coffee plantations, grazing land, and *Shapumba* land. All of them are located in a tropical rainforest area, namely, Pozuzo District, Peru; *Shapumba* land has degraded soils and the other two fields have agricultural soils.

After utilizing TMS and EDXRF we conclude that the iron concentration in the coffee plantations' soils is much higher than in the other two types of soils; the TMS gave us a detailed characterization of the silicates, clay minerals and iron oxides present in these coffee plantations' soils. Besides, we want to stress that sample M-69, from coffee plantations, shows the presence of illite, montmorillonite, and three magnetic sextets S1, S2 and S3; all three sextets are assigned to  $\text{Fe}^{3+}$  from hematite ( $\text{Fe}_2^{3+}\text{O}_3$ ); two of these sextets, S1 and S3, with the lowest hyperfine fields, are related to weakly ferromagnetic hematite in which Fe substitution for Al has taken place showing the effects of a strong weathering in these soils. In regard to grazing land we have found out that a greater concentration of Si, Fe and K exist in these samples. Besides, for *Shapumba* soils, in agreement with the presence of goethite revealed by XRD, doublet D5 is assigned to superparamagnetic goethite whose presence would indicate that these soils are thermodynamically stable; the absence of crops is probably due to its very low pH.

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