

## Organic matter and clay mineral crystallinity in soils of a topossequence on Basalt from Southern Brazil.

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**Abstract.** In this study, the relationship between soil organic matter (SOM) and mean crystallite dimension (MCD) of clay minerals from surface and subsurface horizons from soils of a topossequence in Southern Brazil was evaluated. Soil C and N contents were determined and the SOM chemical composition was evaluated by means of FTIR spectroscopy, after treating the sample with 10% HF solution. The crystallinity of minerals was assessed by X-Ray diffraction that was performed on Fe-oxides free samples and on Fe-concentrated samples. The contents of C and N and the relative intensities of the FTIR spectra were considered as predictor variables and the MCD of hematite, goethite, kaolinite and gibbsite as predicted variables. C and N content and carboxylic and C-O-alkyl groups showed significant effect on the variation of the MCD: the crystallinity of the Fe-oxides and that of kaolinite was inversely affected by these three SOM parameters. In contrast, the MCD of gibbsite was not affected by the SOM parameters. The SOM influence on the crystallinity of Fe-oxides was assigned to surface complexation reactions and to surface redox reactions that promote a continuous dissolution-precipitation process.

### Introduction

Kaolinite (Kt), gibbsite (Gb) and Fe and Al oxides are usually found in tropical and subtropical soils and their abundance in the soil profile is determined by the chemical composition of the parent rock, landscape position and pedogenic stage. The interaction of SOM groups (SOM) with the surface of these minerals may prevent the organic compounds against microbial degradation<sup>(1)</sup>.

The organic groups involved in these interactions depend on the type and characteristics of the mineral surface<sup>(2)</sup>. The surface of Gb shows a high density of bi-coordinated hydroxyl groups on its planar surface, which form most commonly hydrogen bonding and dipole interactions with SOM<sup>(3)</sup>. In comparison, the high density of mono-coordinated hydroxyls on the surface of iron oxides such as hematite (Hm) and goethite (Gt), can lead to the formation of strong interactions, such as inner sphere complex, between the organic groups and minerals<sup>(1, 3)</sup>. On the other hand, these interactions may also affect the crystallinity of the clay minerals, due to the continuous precipitation-dissolution process promoted by the surface complexation<sup>(4)</sup>. Considering the specificity of each mineral surface, it is expected that this effect varies according to the mineral type.

In this context, this study aimed to evaluate the relationship between the contents of C and N and chemical groups of SOM on the crystallinity of clay minerals from surface and subsurface horizons of

soils located in a pedogenetic sequence on basalt in the third plateau Paraná southern Brazil.

### Experimental

The study was conducted with four soils showing different stages of pedogenetic evolution from a topossequence located in Londrina, PR, southern Brazil: i) Rhodic typical Oxisol (LVaf) ; ii) Typical eutrophic Oxisol (LVef) ; iii) typical eutrophic Alfisol (NVef); and iv) typical ferric Chernosol (MTF). In each soil a trench was opened and undisturbed samples were manually and carefully collected (five replicates) of the surface (A) and of the subsurface (B) horizons.

The oxidation of SOM was carried out by treating soil samples with hydrogen peroxide - H<sub>2</sub>O<sub>2</sub> (30 % v/v) in a water bath at 70 °C. The clay minerals were identified by X-ray diffraction (XRD) on Fe-oxides free samples (dithionite-citrate-bicarbonate treated samples) and on Fe-oxides concentrated samples (5 mol L<sup>-1</sup> NaOH treated samples). The mean crystallite dimension (MCD) of Hm and Gt was calculated by determining the width at half-height (WHH) of the reflections (104) and (110) of Hm and (110) of Gt. For Gb and Kt, MCD was calculated for the reflections (002) and (001) respectively, using NaCl as an internal standard to obtain the value of  $\beta$ .

The content of C and N was determined by dry combustion. The FTIR spectroscopy analysis was performed on solid samples previously treated with 10 % HF solution (v/v) with a proportion of 1:100 (sample: KBr) (Shimadzu equipment 8300). The

spectra were obtained in the spectral range of 4000-400  $\text{cm}^{-1}$  with 32 scans and resolution of 4  $\text{cm}^{-1}$ . The experimental data were statistically analysed by canonical redundancy analysis (RDA) in which the SOM parameters (C and N content and relative intensities of the SOM groups in the FTIR spectra) were considered as the matrix of predictor variables and the MCD of the clay minerals as the matrix dependent variables.

### Results and Discussion

Only four attributes related to the SOM showed significant correlation with the clay minerals crystallinity by RDA: C and N content of bulk samples and the relative intensity of the carboxyl ( $1710 \text{ cm}^{-1}$ ) and of the C-O-alkyl groups ( $1075 \text{ cm}^{-1}$ ). The increase of SOM content and of these functional groups promoted the decrease of MCD. The proportion of total variance in the set of dependent variable Y (minerals MCD) that was explained by the predictor variables X (SOM parameters) was 80.61 %.

The relevant effect of the variation of the mineral MCD varied among the analyzed minerals. Correlating the original transformed values Y with the predicted values by the linear model Y (Figure 1) we observe that the effect of the SOM parameters was more pronounced on the variation of the Hm MCD (104 and 110) and of Gt MCD (110) in comparison to that of Kt MCD (001). Furthermore, the Gb MCD (002) was not relevantly affected by the SOM parameters in the employed fit model considering  $P < 0.05$ .

The more pronounced effect of SOM on the crystallinity of Fe-oxides in comparison to that of Gb can be assigned to the higher affinity of organic ligands for Fe than for Al<sup>(6)</sup> and also to the ability of Fe to undergo to redox reactions. Our hypothesis is that the continuous dissolution-precipitation process on the Fe-oxides surface would occur both due to a surface complexation mechanism and due to a surface Fe-redox reaction as well. Furthermore, the significant high density of mono-coordinated hydroxyl groups on iron oxides surface, contrary to that observed in the planar surface of Gb, may enable a more effective formation of surface inner sphere complex with Gt and Hm and thus favoring the dissolution/precipitation mechanism. On the other hand, a surface blocking effect of the surface complexed SOM in preventing the further mineral crystallization process should also be taken into account<sup>(1)</sup>. The interaction between C-O-alkyl groups and iron oxides has been previously observed by other authors<sup>(5)</sup>.

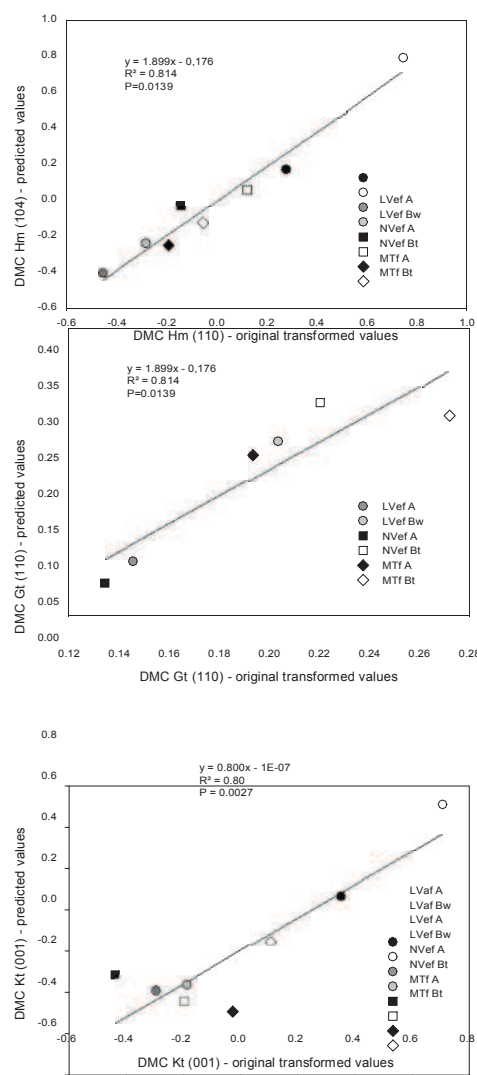
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**Figure 1.** Linear regression between the MDC standardized original values and MDC values predicted by canonical redundancy analysis, using C and N content, relative intensity of COOH ( $1710 \text{ cm}^{-1}$ ) and C-O-alkyl ( $1075 \text{ cm}^{-1}$ ) groups as predictor variables for Hm (104), Gt (110) and Kt (001).