XXXIV CONGRESSO BRASILEIRO DE CIÊNCIA DO SOLO
28 de julho a 2 de agosto de 2013 | Costão do Santinho Resort | Florianópolis | SC

Soil S fractions in Oxisols affected by land use and phosphogypsum application [1]

Susana Churka Blum[2]; Dawit Solomon[3]; Johannes Lehmann[4]; Eduardo Fávero Caires[5]; Luís Reynaldo Ferracciú Alleoni[6]

[2]CAPES/PNPD Postdoctoral Research Fellow; Universidade Federal do Ceará (UFC); Fortaleza, CE; Brasil; sschurka@yahoo.com.br; [3] Senior Research Associate; Cornell University; Ithaca, NY, USA; ds278@cornell.edu; [4] Professor; Cornell University; Ithaca, NY, USA; cl273@cornell.edu; [5] Associate Professor; Universidade Estadual de Ponta Grossa (UEPG); Ponta Grossa; PR; Brasil; efcaires@uepg.br; [6] Associate Professor; ESALQ/USP; Piracicaba, SP, Brasil; alleoni@usp.br.

ABSTRACT: Little information is available regarding the speciation and dynamics of organic sulfur (S) functionalities in highly weathered Brazilian soils. We carried out this study in order to assess the effect of phosphogypsum (PG) application on the form and distribution of organic S pools in soils under no-tillage (NT) and under a native forest site. Solid-state X-Ray Near Edge Structure (XANES) spectroscopy technique was used in the humic substances extracted by 0.1 M NaOH/0.4 M NaF. For all sites and all depths evaluated, reduced and intermediate S species (S^0 to S^{5+}) were dominant when compared to the strongly oxidized ones (S^{6+}). More oxidized S species (sulfate ester - S^{6+}) were present in the forest area and in the PG area (rate of PG = 12 t ha^{-1}) in comparison with the control treatment (cropped area without PG application). Changes in land-use practice altered both qualitative composition and distribution of S functional groups in this humid subtropical Brazilian soil under NT. The use of amendments containing S like PG seems to be vital for the recovery of some S moieties.

Key-words: XANES; phosphogypsum; no-tillage system.

INTRODUCTION

Soil is the primary component of the global biogeochemical cycling of sulfur (S) and acts as a source and a sink for various S species, thus mediating changes of oxidation states (Wang et al., 2006). Therefore, knowledge of S cycling is a key component to understanding changes in the biosphere (Zhao, 1996; Solomon et al., 2005).

Phosphogypsum (PG) is a valuable source of S and provides this nutrient to plants as SO_4^{2-}. However, there are not detailed investigations on the role of PG in the biogeochemical cycling of S in the wet tropics. Also, there is not enough information about this soil amelioration practice in Brazilian no-tillage (NT) systems. This knowledge is vital to effectively describe S fluxes from various pools of Brazilian soils to design and to promote sustainable agricultural systems in the country. It also helps to better evaluate the transfer of S between the soil environment and other reservoirs during the biogeochemical S cycle in the tropical agro-ecosystems following PG-based soil amelioration (Schroth et al., 2007; Solomon et al., 2009).

Although S is present mainly in organic forms in soils (>95%), very little is known about the identities of these specific S containing molecules, especially in humid tropical soils. Most recently, studies using noninvasive synchrotron-based sulfur K-edge X-ray Near-edge Structure (XANES) spectroscopy have been successfully employed to identify multiple S fractions in a variety of environmental and geochemical samples. XANES provides specific information on the functional groups containing S because of the sensitivity to the electronic structure, oxidation state, and the geometry of the neighboring atoms (Vairavamurthy et al., 1997). The advantage XANES affords over traditional wet-chemical methods is that intermediate oxidation states can be identified. In the present study, we assessed (i) the impacts of land use changes comparing undisturbed native forest and no-tillage systems on the S forms, and (ii) the role of PG application in NT systems on form and distribution of organic S pools in soils in NT-based agricultural systems of Brazil using XANES technique.

MATERIAL AND METHODS

The study was carried out using soil samples collected from a PG field experiment in a cropped area in the southern Brazil (Guarapuava, state of Parana - 25°17' S and 51°48' W, 997m a.s.l.) and also from a native forest near the cultivated area, considered a reference of undisturbed system. Soil is a clayey Typic Hapludox, and the main characteristics of the soil are presented in **table 1**.

2

XXXIV CONGRESSO BRASILEIRO DE CIÊNCIA DO SOLO
28 de julho a 2 de agosto de 2013 | Costão do Santinho Resort | Florianópolis | SC

Table 1 - Selected properties of the Oxisol (0-20cm) collected in a cropped area under NT and under a native forest (NF) in the southern Brazil (TOC = total organic carbon; TN = total nitrogen content; C = carbon; N = nitrogen; S = sulfur))

Soils	pH 0.01 M CaCl$_2$	Total S	TOC	TN	C/N	C/S	N/S
		mg kg^{-1}	g kg^{-1}				
NT	5.9	329.3	35.6	1.9	18.8	108.1	5.8
NF	4.5	459.5	41.9	2.8	14.8	91.2	6.1

Solid-state characterization by XANES spectroscopy of S oxidation states in the humic substances extracted from the soils was carried out using S K-edge XANES spectroscopy at beam-line X-19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The extraction procedure for the humic fraction followed the outline of Schnitzer (1982) modified by Sumann et al. (1998). Experimental data at X-19A were collected under standard operating conditions. The X-ray energy were calibrated to the K-edge of elemental S at 2473 eV and scans ranging from 80 eV below to 150 eV above the absorption edge of S were collected with step size of 0.2 eV. We used a monochromator consisting of double-crystal Si (111) with an entrance slit of 0.5 mm and a minimum energy resolution of 2 x 10^{-4}($\approx$ 0.5 eV) at the S K-edge. Background correction and normalization of the spectra were performed using the software WinXAS and the deconvolution of XANES spectra for each sample into pseudocomponents was accomplished by the nonlinear last-squares fitting routine SOLVER supplied with Microsoft Excel following Solomon et al. (2003; 2005; 2009; 2011) and Xia et al. (1998).

RESULTS AND DISCUSSION

The white-line of sulfur increased with the formal oxidation number of the sulfur ion in our study and the peak positions varied from 2473.4 eV to 2483.4 eV. Our baseline-corrected and normalized XANES spectral features recorded from soil humic fractions consistently had several white-lines in the energy range of 0 to 10 eV above the S K-edge (**Figure 1**).

In all treatments evaluated, the proportion of C-bonded and ester S was not strongly affected by depth, but reduced and intermediate S species (S^0 to S^{5+}) dominated over the strongly oxidized ones (S^{6+}) in all areas evaluated in this experiment (**Table 2**). The first groups of organic S compounds -

reduced and intermediate S species represent S directly linked to C in C-S or C-S-O linkages, as in the case of S-containing amino acids and sulfonates, respectively. They are commonly referred to as C-bonded S in the conventional classification systems. On the other hand, S in highly oxidized state denotes organic S compounds where S is linked to C mostly through O atoms in the form of C-O-S linkage, as in the case of true ester sulfates (C-OSO$_3$-C).

At the native forest site, C-bonded species (more than 60%) prevailed in all depths evaluated. After the adoption of NT cultivation, we observed 15% reduction in these S forms of highly reduced and intermediate states with increase in ester-S (**Table 2**). Losses of C-bonded S due to cultivation are broadly reported in the literature (Solomon et al., 2003; 2011), and they occur due to soil disturbance, stimulated aerobic decomposition process and exposed physically protected organic S to microbial attack.

By using XANES technique, however, we were not able to see strong differences in ester-S with the application of PG. Small increased on ester-S with PG application were observed in the first depths of the soil collected under NT system. One of the biggest critics concerning XANES spectroscopy is that it is generally applied to humic substances in order to improve the signal, since large background are verified when S XANES spectra is measured directly from the bulk soils, what makes very difficult the quantification of S species by standard programs (Solomon et al., 2003). The use of soil extracts may not reflect the in situ speciation of S in soil (Eriksen, 2009) and some artificial changes, like hydrolysis reactions or autoxidation can occur during alkali extractions (Shoenau and Bettany, 1987), demanding more caution when interpreting the results (Anderson and Shoenau, 1993). However, studies using S K-edge XANES (Hutchinson et al. 2002) failed to detect any change in the oxidation states, as well as accompanying structural composition of organic S in humic substances extracts aerated at various pH levels for up to 44 h. The dominance of the C-S in the soil extracts observed in our study is in agreement with another researchers that used XANES spectroscopy applied to humic substances (Martinez et al., 2002; Prietzel et al., 2003; Solomon et al., 2003; 2005; 2009; 2011; Xia et al., 1998), and revealed that S directly linked to C is the predominant form of organic S functional groups.

3

XXXIV CONGRESSO BRASILEIRO DE CIÊNCIA DO SOLO
28 de julho a 2 de agosto de 2013 | Costão do Santinho Resort | Florianópolis | SC

CONCLUSIONS

Sulfur in more reduced and intermediate states are the predominant forms of S in both forest and NT-cropped systems. A reduction of C-bonded S in NT compared to the forest and S was verified reinforcing the role of this S functionalities .

Changes in land-use practice and PG application alter both quantitative and qualitative composition of S functional groups in this wet subtropical Brazilian soil under NT. The use of soil amendments containing S seems to be vital for the recovery of S moieties.

ACKNOWLEDGEMENTS

REFERENCES

ANDERSON, D.W. & SHOENAU, J.J. Soil Humus Fractions. In: CARTER, M.R., ed. Soil sampling and methods of analysis. Boca Raton: Lewis Publishers, 1993. p. 391-395.

ERIKSEN, J. Soil sulfur cycling in temperate agricultural systems. Advances in Agronomy, 102: 55-89, 2009.

HUTCHINSON, K.J., HESTERBERG, D., CHOU, J.W. Stability of reduced organic sulfur in humic acid as affected by aeration and pH. Soil Science Society of America Journal, 65: 704–709, 2002.

MARTÍNEZ, C.E., MCBRIDE, M.B., KANDIANIS, M.T. et al. Zinc–sulfur and cadmium–sulfur association in metalliferous peats: evidence from spectroscopy, distribution coefficients, and phytoavailability. Environmental Science and Technology, 36: 3683–3689, 2002.

PRIETZEL, J., THIEME, J, NEUHÄUSLER, U. et al. Speciation of sulfur in soils and soil particles by X-ray spectromicroscopy. European Journal of Soil Science, 54: 423-433, 2003.

SCHNITZER, M. Organic matter characterization. In: PAGE, A. L.; MILLER, B.L.; KENEY, R.H., eds. Methods of soil analysis. Madison: ASA, SSSA, 1982. p. 581-594.

SCHOENAU, J.J. & BETTANY, J.R. Organic matter leaching as a component of carbon, nitrogen, phosphorus, and sulfur cycles in a forest, grassland and gleyed soil. Soil Science Society of America Journal, 51: 646-651, 1987.

SCHROTH, A.W., BOSTICK, B.C., GRAHAM, M. et al. Sulfur species behavior in soil organic matter during decomposition. Journal of Geophysical Research, 12: 1-10, 2007.

SOLOMON, D., LEHMANN, J., KINYANGI, J. et al. Antropogenic and climate influences on biogeochemical dynamics and molecular-level speciation of soil sulfur. Ecological Applications, 19: 989-1002, 2009.

SOLOMON, D., LEHMANN, J., LOBE, I. et al. Sulphur speciation and biogeochemical cycling in long-term arable cropping of subtropical soils: evidence from wet-chemical reduction and S K-edge XANES spectroscopy. European Journal of Soil Science, 56: 621-634, 2005

SOLOMON, D., LEHMANN, J., MARTÍNEZ, C.E., 2003. Sulfur K edge x-ray absorption near-edge structure (XANES) spectroscopy as a tool for understanding S dynamics. Soil Science Society of America Journal, 67: 1721–1731, 2003.

SOLOMON, D., LEHMANN, J., ZARRUK, K.K. et al. Speciation and long-and short-term molecular-level dynamics of soil organic sulfur studied by X-ray Absorption Near-Edge Structure Spectroscopy. Journal of Environmental Quality, 40: 704-718, 2011.

SUMANN, M., AMELUNG, W., HAUMAIER, L. et al. Climatic effects on soil organic phosphorus in the North American Great Plains identified by phosphorus-31 nuclear magnetic resonance. Soil Science Society of America Journal 62: 1580–1586, 1998.

VAIRAVAMURTHY, A., MALETIC, D., WANG, S., et al. Characterization of sulfur-containing functional groups in sedimentary humic substances by X-ray absorption near-edge spectroscopy. Energy & Fuels, 11: 546-553, 1997.

WANG, J., SOLOMON, D., LEHMANN, J. et al. Soil organic sulfur forms and dynamics in the Great Plains of North America as influenced by long-term cultivation and climate. Geoderma, 133: 160-172, 2006.

XIA, K., WEESNER, F., BLEAM, W.F. et al. XANES studies of oxidation states of sulfur in aquatic and soil humic substances. Soil Science Society of America Journal 62, 1240-1246, 1998.

ZHAO, F.J., WU, J., MCGRATH, S.P. Soil organic sulphur and its turnover. In: PICCOLO, A, ed. Humic Substances in Terrestrial Ecossystems. Amsterdan: Elsevier, 1996, p. 467-506.

XXXIV CONGRESSO BRASILEIRO DE CIÊNCIA DO SOLO
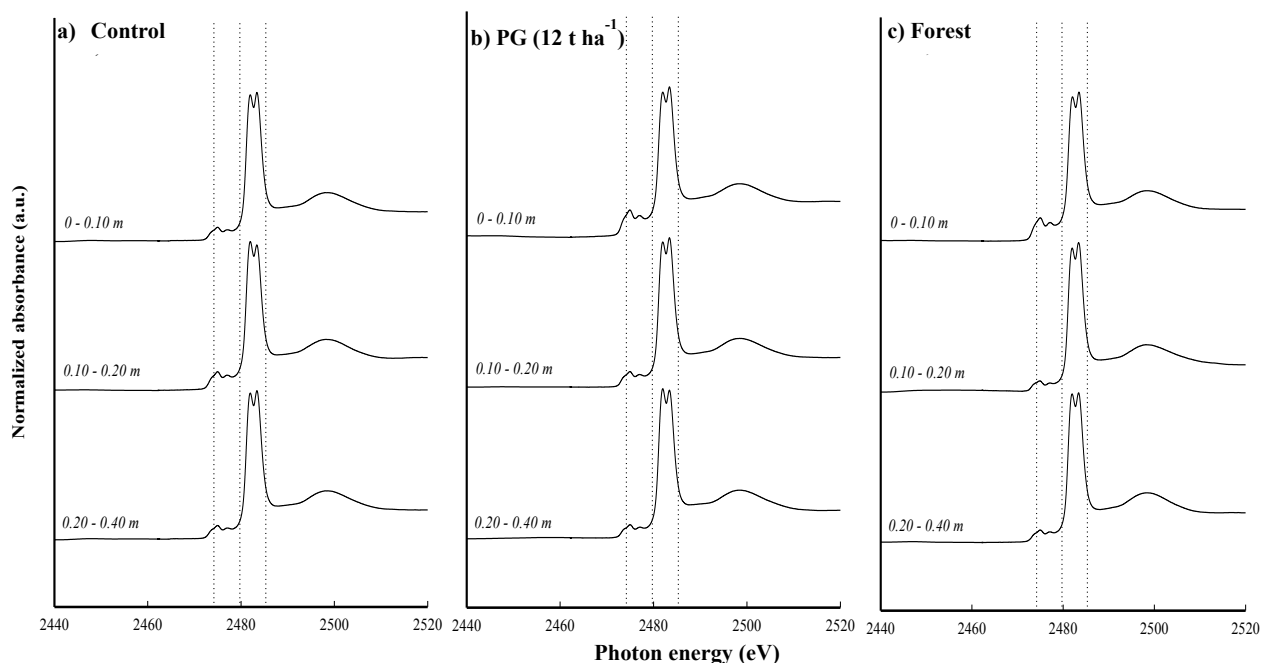28 de julho a 2 de agosto de 2013 | Costão do Santinho Resort | Florianópolis | SC

Figure 1. S K-edge XANES spectra of the humic extracts of soils collected under native forest and under no-tillage system with and without phosphogypsum application in Guarapuava, Paraná, Brazil.

Table 2 - Relative abundance of S species at electronic oxidation states in humic substances extracted from Oxisols under native forest (NF) and under no-tillage system with (NT+PG) and without phosphogypsum application (NT) in Guarapuava, Paraná, Brazil.

Land use	G1[#]	G2	G3	G4	G5	*C-bonded*	*Ester-S*
				.........%.........			
0-0.10 m							
NT	13.31	0.87	18.53	24.43	42.86	*57.1*	*42.9*
NT+PG	19.71	0.78	10.10	24.40	45.02	*55.0*	*45.0*
NF	16.73	3.38	29.54	21.50	28.85	*71.1*	*28.9*
0.10-0.20m							
NT	9.10	1.31	14.73	28.91	45.95	*54.0*	*46.0*
NT+PG	12.27	0.00	11.09	29.65	47.00	*53.0*	*47.0*
NF	7.21	0.84	30.24	26.59	35.11	*64.9*	*35.1*
0.20-0.40m							
NT	6.86	0.50	19.38	25.34	47.91	*52.1*	*47.9*
NT+PG	10.63	0.00	14.73	33.00	41.63	*58.4*	*41.6*
NF	8.47	9.34	23.33	36.49	22.37	*77.6*	*22.4*

Gaussian curves, representing the oxidation states of the S atom.