Geoderma 200-201 (2013) 156–164

Contents lists available at SciVerse ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Sulfur forms in organic substrates affecting S mineralization in soil ☆

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ARTICLE INFO

Article history:
Received 8 November 2012
Received in revised form 6 February 2013
Accepted 9 February 2013
Available online xxxx

Keywords:
Wet-chemical S fractionation
Ester-S
C-bonded S
Plant residues
Biochar
XANES

ABSTRACT

The effects of sulfur (S) forms beyond total S contents for S release from litter to soil are not well understood. In this study, the effect of plant residues (black oat — *Avena strigosa* Schreb, pea — *Pisum sativum* L., rape — *Raphanus raphanistrum* L., wheat — *Triticum aestivum* L., corn stalk — *Zea mays* L. and corn stalk biochar applied on an equivalent sulfur basis) with greatly varying S contents, C/S ratios and organic S forms on S mineralization and immobilization in an Oxisol was monitored for 90 days using a laboratory incubation experiment. Soil microbial activity (CO_2 evolution) and N mineralization were also evaluated. At 3 and 90 days of the incubation experiment, the samples were analyzed to assess the main transformations in the soil S pools. Plant residues and biochar had a considerable effect on S mineralization. The highest leaching of sulfate occurred after the application of biochar (11.05 mg kg^{-1} at the first leaching, corresponding to 29.1% of the total S added), and the main mechanisms involved in this process were the abiotic release of mineral sulfur and the hydrolysis of ester-S mediated by soil enzymes, since no relationship with CO_2 evolution was observed. Our results suggest that the forms of S in the starting materials seem to drive S mineralization. Increases in mineralized S at earlier stages of the incubation after the incorporation of plant residues and biochar to the soil were correlated with the most oxidized S species (+6) in the organic amendments as revealed by X-ray Absorption Near-Edge Structure (XANES) spectroscopy ($r = 0.92$, $p < 0.01$ at 15 days and $r = 0.80$, $p < 0.05$ at 30 days; $n = 6$). These findings seem to confirm the hypothesis that S forms rather than S concentration in the tissue plays a major role in S mineralization. In addition, during the first three days of incubation an increase of soil contents of ester-S was associated with a decrease in C-bonded S. Our results, obtained by wet-chemical S fractionation, indicated that in highly oxidized S containing residues, the process of S mineralization was mostly governed by the enzymatic hydrolysis of the ester-S pool rather than the need for carbon to provide energy to the microorganisms. With the application of C-bonded S rich residues, the dominant mechanism was biological mineralization, thus liberating S as a secondary product.

1. Introduction

Sulfur (S), along with nitrogen (N) and phosphorus (P), is responsible for the synthesis of proteins and for a number of essential vitamins and cofactors (Kertesz and Mirleau, 2004). It is not only an often growth-limiting plant nutrient but also indirectly affects the use efficiency of other plant nutrients, such as N (De Bona and Monteiro, 2010). In fact more recently, S deficiency to plants has been reported in several parts of the world (Kost et al., 2008; Scherer, 2009) mainly occurring due to: (i) the reduction of sulfur dioxide emission in the past decades (Lehmann et al., 2008), (ii) the use of highly concentrated fertilizers containing little or no S, and (iii) the increased S removal from soils under intensive cropping systems and increased crop yields. Therefore, predicting the supply of S from the soil to crops or assessing the effect of organic substrates addition on S mineralization requires an understanding of the forms of S and its transformations in soils (Zhao et al., 2006).

Most of the S in soils is bound to organic molecules, making up more than 90% of the S present in soils (Eriksen, 2009; Neptune et al., 1975; Solomon et al., 2001, 2005, 2009). Inorganic S generally accounts for less than 10% of total S in temperate (Eriksen, 2009) and humid tropical soils (Neptune et al., 1975; Solomon et al., 2001, 2009). Despite the fact that plants absorb S mainly as sulfate, organic S (S directly bonded to C and ester S) pools are important sources of S to plants during their growing season (De Bona and Monteiro, 2010; Freney et al., 1975; Goh and Pamidi, 2003; McGill and Cole, 1981). The process of transformation

☆ Part of the doctoral thesis of the first author.

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http://dx.doi.org/10.1016/j.geoderma.2013.02.003

of organic S to inorganic sulfate (mineralization) and the reverse process (incorporation of sulfate into soil organic compounds or immobilization) play important roles in the cycling of S within the soil and are microbiologically mediated (Kertesz and Mirleau, 2004).

Sulfur mineralization in the soil is typically attributed to either biological or biochemical processes (McGill and Cole, 1981). The biological route is governed by the search for energy and the S is released as a by-product. The biochemical process is defined as the release of S from ester sulfates, through extracellular enzymatic hydrolysis (McGill and Cole, 1981). Even though these two pathways have been described for some time, S mineralization is often rather related to initial S concentrations (Janzen and Kucey, 1988), than to S forms (Singh et al., 2006) in plant residues. Singh et al. (2006) hypothesized that the observed rapid release of sulfate immediately after addition of canola (*Brassica napus*) residues was not only a result of the total S contents but also of the form of S present in its tissues (soluble sulfate and readily degradable organic S forms). However, a systematic comparison between residues containing different forms of S has not been done. Moreover, most S dynamics studies conducted in the past were limited by the crude analytical techniques employed for its speciation, since the characterization of S species in a mixture represents a challenge (Jalilehvand, 2006). Most recently, studies using noninvasive synchrotron-based S K-edge X-ray Near-Edge Structure (XANES) spectroscopy have been successfully used to identify multiple S moieties in a variety of environmental and geochemical samples, including marine sediments, soils and soil extracts. However, only few studies have been conducted to study S speciation and the processes of S mineralization and immobilization using this approach (Solomon et al., 2011; Zhao et al., 2006). To the best of our knowledge, until now, no studies have been performed combining structural information of the plant residues S using XANES with S release dynamics.

Therefore, the objectives of this study were to investigate S mineralization and immobilization in soils affected by plant residues with different S forms. Such studies will provide valuable information for modeling of S transformations in soil and for management of crop residues to address S deficiency.

2. Material and methods

2.1. Soil samples

The soil samples chosen for this experiment came from a clayey Typic Hapludox in southern Brazil (Guarapuava, State of Parana — 25°17′ S and 51°48′ W, 997 m a.s.l.) that has been cultivated under no-till (NT) system for 19 years in comparison to soil collected from a forest site adjacent to the cultivated area. The cultivated area showed high crop grain yields in the last years due to the adoption of improved crop varieties, best management practices and appropriate nutrient inputs (as Ca and Mg provided by liming and P and K by periodic fertilization), but the soil S content remained low since no S had been applied in the past years. Samples (0–0.05 m) were collected in October 2010 from the forest area and from the control plots of an experiment that evaluated the benefits of phosphogypsum application (Caires et al., 2011) on soils and crops in rotation. The forest site consisted of a fragment of the ombrophilous (high-rainfall tolerant) mixed forest dominated by Parana Pine (*Araucaria angustifolia*) also referred to as *Araucaria* forest (Veloso et al., 1991). Samples at a depth of 0–0.05 m were taken since it is the layer most affected by the deposition of plant residues in NT. The soils were sieved (through a 2-mm sieve), dried at 40 °C and brought to the laboratory, where a small portion was separated for basic characterization. The mineralogy mainly constituted of gibbsite and kaolinite, with presence of hematite, goethite, and some clay minerals with hydroxyinterlayers. Soils had 592, 311 and 98 g kg^{-1} of clay, silt and sand, respectively; 168.0 g kg^{-1} of dithionite–citrate–bicarbonate ("free") extractable Fe; 5.2 g kg^{-1} of oxalate ("amorphous") extractable Fe and 10.7 g kg^{-1} of oxalate extractable Al. Other properties of both sites are shown in Table 1. The pH was measured in a 0.01 M $CaCl_2$ solution (soil solution ratio of 1:2.5 w/v). Organic C and total N were measured by dry combustion in a Thermo-Finnigan Flash 1112 elemental analyzer. Total S was obtained by alkaline digestion with NaOBr (Tabatabai and Bremner, 1970) and colorimetrically quantified as bismuth sulfide (Kowalenko, 1993a). Sulfate was extracted by 0.01 M $Ca(H_2PO_4)_2 \cdot H_2O$ (Fox et al., 1964) and also determined by colorimetry as bismuth sulfide.

2.2. Plant residues

Fresh (black oat — *Avena strigosa* Schreb, pea — *Pisum sativum* L., rape — *Raphanus raphanistrum* L., wheat — *Triticum aestivum* L., and corn stalk — *Zea mays* L.) and pyrolyzed (corn stalk biochar) crop residues were used in this study. Plant residues were dried at 60 °C, ground (<2 mm) with a Wiley mill and sealed in plastic bags before use. The biochar was produced using slow pyrolysis (Daisy Reactor, Best Energies, Inc., Cashton, WI, USA). Approximately 3 kg of feedstock were manually placed into the reactor, which was thoroughly purged with N_2 (with the mixer running). The material was charred for 80–90 min, including raising the temperature to the target with a few degrees per minute and holding at final temperature (450 °C) for 15–20 min. Subsequently, the furnace was turned off, and the main chamber was allowed to cool before collecting the biochar under N_2 purge to reduce rapid oxidation (leading to a more homogeneous product) and auto-ignition.

A portion of each residue was analyzed for some basic properties (Table 2). Contents of total C and N were measured by dry combustion using a CN-2000 (Leco Corporation, St. Joseph, MI, USA), and total S content was determined by nitric–perchloric digestion and measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro Ciros, Spectro A.I. Inc. MA, USA). An S equivalent of 38 mg S kg^{-1} soil was applied (corresponding to 10% of the total S present in the soil) as plant residues or biochar. As the concentrations of S vary in the plants and in the biochar, the amounts of residue applied to the soil followed a wide range of quantity varying from 3 g kg^{-1} of soil (rape) to 88 g kg^{-1} of soil (corn stalk). A pyrolyzed residue was included as an extreme form of organic matter addition of low C mineralizability but similar C/S ratio to the unpyrolyzed corn (Table 2).

Solid-state characterization of S oxidation states in plant samples and corn biochar was carried out using S K-edge XANES spectroscopy at beam-lines X-19A and X-15B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The samples were homogeneously mixed and finely ground using a ball grinder before

Table 1
Selected properties of the Oxisols collected from a cultivated area under NT and an adjacent forest in southern Brazil.

Soils	pH $CaCl_2$	Total S	S $Ca(H_2PO_4)_2$	Organic C	Total N	C/N	C/S	N/S
		mg kg^{-1}		g kg^{-1}				
Agricultural area	5.3	380.9	2.6	43.5	2.6	16.7	114.2	6.8
Natural forest area	4.8	532.7	14.6	60.1	4.2	14.3	112.8	7.9

Table 2
Selected properties of the materials used as sources of S.

Materials	Total C	Total N	Total S	C/N	C/S	N/S
	g kg^{-1}					
Black oat	438.7	11.5	1.1	38.1	409.9	10.7
Wheat	437.3	11.1	1.4	39.5	308.4	7.8
Pea	435.6	31.9	1.8	13.7	239.3	17.5
Rape	414.8	30.0	11.1	13.8	37.3	2.7
Corn stalk	426.2	5.3	0.4	80.4	991.2	12.3
Corn stalk biochar 450 °C	673.0	11.2	0.8	60.3	851.8	14.2

the measurements. Experimental data at X-19A from the plant samples were collected under standard operating conditions. The X-ray energy was calibrated to the K-edge of elemental S at 2472.7 eV (Vairavamurthy et al., 1997) and scans ranging from 80 eV below to 150 eV above the absorption edge of S were collected with a step size of 0.2 eV. A monochromator consisting of double-crystal Si (111) with an entrance slit of 0.5 mm and a minimum energy resolution of 2×10^4 ($\approx$0.5 eV) at the S K-edge was used. The monochromator was detuned to 70% at the S K edge in order to reduce fluorescence induced by high-order harmonics (Xia et al., 1998). The spectra were recorded in fluorescence mode using a passivated implanted planar silicon (PIPS) detector (Canberra Industries, Meriden, Connecticut, USA). The beam path from the incident ion chamber to the sample chamber was purged with He gas. The samples were mounted to a 0.5-mm thick acrylic holder and covered with a 3.6-μm thick S-free Mylar film (Chemplex Industries, Palm City, Florida, USA).

At X-15B, data from the biochar sample were directly recorded under standard operating conditions, using the calibration and step sizes described above. We used a monochromator consisting of two parallel Si (Trust and Fry, 1992) crystals with an entrance slit of 0.5 mm and with a minimum energy resolution of 2×10^4 ($\approx$0.5 eV) at the S K-edge. High-order harmonics were eliminated by using a collimating/harmonic-rejection mirror upstream of the monochromator, rather than by detuning the monochromator. Beam was then focused to a 1-mm spot size in the sample. The beam path remained in ultra-high vacuum (UHV) up to an ultra-thin Be window; the atmosphere in the sample chamber was He. Incident beam intensity was measured using a windowless He-filled ionization chamber. The spectrum was recorded in fluorescence mode using a Canberra Ge detector (Canberra Industries, Meriden, Connecticut, USA) positioned 90° to the incident beam. The sample was accommodated in a thin S-free polypropylene film (5 μm thick) for XRF (Spex CertiPrep, Metuchen, NJ, USA) and attached to a thick paper sample holder.

Background correction and normalization of the obtained spectra were done using the software WinXAS according to Martínez et al. (2002), Solomon et al. (2003, 2005, 2009, 2011) and Xia et al. (1998). Deconvolution of XANES spectra for each sample into pseudocomponents was accomplished by the nonlinear least-squares fitting routine SOLVER supplied with Microsoft Excel. XANES spectra were fitted using a series of Gaussian peaks (G1, G2, G3, G4 and G5) and arctangent functions (AT1 and AT2). The Gaussian curves correspond to different oxidation states and organic S forms (Solomon et al., 2003; Xia et al., 1998). The first (AT1) and the second (AT2) arctangent functions represent the transition of ejected photoelectrons to the continuum for the unoxidized S and for the oxidized-S forms. We used the sum of these two arctangent functions (AT1 and AT2) to approximate the X-ray absorption step heights (background) of the spectra. The energy positions (eV) of the Gaussian curves were used to identify the oxidation states of S present in the sample and the peak areas were used to calculate the percentage of S present at each oxidation state (Martínez et al., 2002; Solomon et al., 2003, 2005, 2009, 2011; Xia et al., 1998). Assumptions used in the fitting process, according to Xia et al. (1998) were: (i) at least four major components are present in each spectrum, with additional components added in the fitting process until a satisfactory fitting was obtained; (ii) all components with s → p transition peaks are Gaussian; (iii) the full width at a half maximum (FWHM) of each Gaussian component for low-valent S ($\leq +4$) is loosely constrained between 0.2 and 1.0 eV, while the FWHM of Gaussian components for sulfonate ($+5$) and sulfate ($+6$) are tightly constrained at 1.4 ± 0.2 and 2.2 ± 0.2 eV, respectively (0.2 eV is the uncertainty of the energy calibration; 1.4 and 2.2 are the FWHM for sulfonate and sulfate model compounds, respectively); and (iv) the X-ray absorption step heights (background) of the XANES spectra are approximated by the sum of two arctangent weighted functions.

2.3. Experimental procedure and analytical techniques — incubation and CO_2 evolution

The experiment was conducted using an "open" incubation system (Ghani et al., 1992; Janzen and Kucey, 1988; Maynard et al., 1983; Stanford and Smith, 1972; Tabatabai and Al-Khafaji, 1980) that better represents the removal of nutrients by plants and the leaching processes of these elements under moist field conditions (Tabatabai and Al-Khafaji, 1980), compared to "closed" incubation systems. We used 106-mL modified PVC filter units that were built by attaching a nylon mesh sheet (250 μm opening) between two pieces of a PVC tube (Supplementary Fig. S1). A glass microfiber filter (VWR Scientific Products, West Chester, PA) and glass wool were added to the bottom of the PVC filter unit to help with drainage. Fifty grams of soils (collected under NT and forest and passed through a 2-mm sieve) were homogeneously mixed with pre-acid washed sand (250–350 μm) in a 1:1 proportion (oven-dry basis). Fresh and pyrolyzed crop residues (black oat, pea, rape, wheat, corn stalk and corn stalk biochar) were mixed into the soil (collected under NT) and the water content was adjusted to 75% of the moisture content at field capacity (Ghani et al., 1992). The mixture was placed into PVC cylinders with a bulk density of 1.3 g cm^{-3}. The experiment was arranged in a completely randomized design with three replicates. A total of 24 experimental units (eight residues — black oat, pea, rape, wheat, corn stalk and corn stalk biochar; one control — soil collected under NT; one forest soil used as a reference for comparison with the control, since it was an undisturbed system with higher contents of organic and inorganic S, in three replicates) plus four blanks (the funnel setup used for the experiment, but without soil or plant material) were placed into 500-mL sealed Mason Jars filled with 50 mL of deionized water in the bottom to maintain a water-saturated atmosphere (since the jars were periodically opened to collect the NaOH used to trap microbially respired CO_2) (Supplementary Fig. S1). The sealed jars were incubated at 30 °C in the dark. The HCO_3^- and CO_3^{2-} ions present in the 2 mL NaOH were precipitated with $BaCl_2$ solution, and total respired CO_2–C was determined by titrating the residual NaOH with 0.1 M HCl using phenolphthalein as an indicator.

2.4. Nitrogen and sulfur mineralization

The PVC cylinders were mounted on top of the filter units and mineral N and S were obtained by periodic leaching events using 100 mL of 0.01 M $CaCl_2$ (in consistent 10 mL increments) and removing the excess water by vacuum filtration (600 mm Hg) (Supplementary Fig. S1). Leachates were collected after 15, 30, 60 and 90 days of incubation. A thin pad of glass wool was placed on top of the soil to avoid soil disturbance during the addition of water. The extracts were passed through a Whatman number 42 filter paper (Whatman International, England) during vacuum filtration and then filtered using a 0.45-μm pore membrane (Pall Gelman Laboratory, Ann Arbor, Michigan, USA). Contents of SO_4^{2-}, NO_3^- and NO_2^- were determined by ion chromatography and the content of NH_4^+ was determined by the Indophenol Blue colorimetric method (Keeney and Nelson, 1982).

Since the amount of applied organic matter was adjusted to its S content, we normalized the C or N mineralization by the sum of C or N added (via plant or biochar) and the amount already existing

in the soil (control treatment). We applied a curve fitting to the accumulated mineralized data of C, N and S using a double-exponential model (Kalbitz et al., 2005) using the routine Solver supplied by MS-Excel. The equation used to fit the cumulative C, N and S mineralized was:

$$X_t = X_1\left(1-e^{-k}1^t\right) + (1-X_1)\left(1-e^{-k}2^t\right)$$

where: X_t = mineralized C, N or S; X_1 = size of the labile pool; $1-X_1$ or X_2 = size of the stable pool; k_1 and k_2 = mineralization rates of the labile and stable pools, respectively; and t = time of incubation (days).

2.5. Sulfur fractionation

At 0, 3 (peak of microbial activity, Supplementary Fig. S3), and 90 days of incubation, we collected soil samples to perform the S fractionation according to Kowalenko (1993a,b) and obtained the following fractions: sulfate-S, ester-S and C-bonded S. Total S was obtained by alkaline digestion (Tabatabai and Bremner, 1970) and quantified according to Kowalenko (1993b). Soluble plus adsorbed S was extracted with 0.01 M $Ca(H_2PO_4)_2 \cdot H_2O$ and measured by colorimetric method as bismuth sulfide. Total organic S was calculated as the difference between total S and phosphate-extractable S. Ester-S was determined using HI digestion/distillation (Kowalenko, 1993b), corrected for phosphate-extractable S. Carbon-bonded S was calculated as the difference between total organic S and ester-S.

2.6. Statistical analysis

All data were tested for normality using SigmaPlot v11 (Systat Software Inc., Chicago, IL). Analysis of variance (ANOVA) was carried out to determine the effects of organic substrates on cumulative C, N and S mineralization. Where the ANOVA indicated significant main effects, they were further analyzed using a Tukey test ($p<0.05$). Pearson Product Moment correlations and multiple regressions were used to explain the relationship between mineralization patterns and plant/biochar composition.

3. Results

3.1. C, N and S mineralization

Soil microbial activity, monitored as CO_2 evolution, varied widely among the treatments (Fig. 1). During the 90 days of incubation, the cumulative amounts of CO_2 evolved ranged from 2.65 (control) to 10.21 g kg^{-1} (corn stalks) (Supplementary Table S1). CO_2 evolution increased in the untreated soils (without organic substrates) during the 90 days of the incubation, and was higher in the forest soil compared to the cultivated area ($p<0.05$). CO_2 production varied broadly among the plant residues and the biochar. Highest rates were observed in wheat and oat residues, followed by pea, corn stalk and rape. After normalizing the C mineralization based on the amount of C added, the fraction of C emitted by the treatment that had received biochar was lower than the control treatment, for all days of evaluation. Differences between corn stalk biochar and the untreated soil ($p<0.05$) were only found during the first four days of the incubation (Supplementary Table S1), during which the biochar caused little increase in CO_2 evolution. Oat, wheat and pea showed higher labile C pools obtained by curve fitting compared to the other residues and the soils that did not receive organic substrate additions (Table 3). Modeled stable C pools were higher for biochar than the other treatments (Table 3). Decomposition of rape plants, added in lower amounts compared to the other residues, resulted in a high kinetic loss constant of the labile pool, which represented 4.8% of the mineralized C (Table 3).

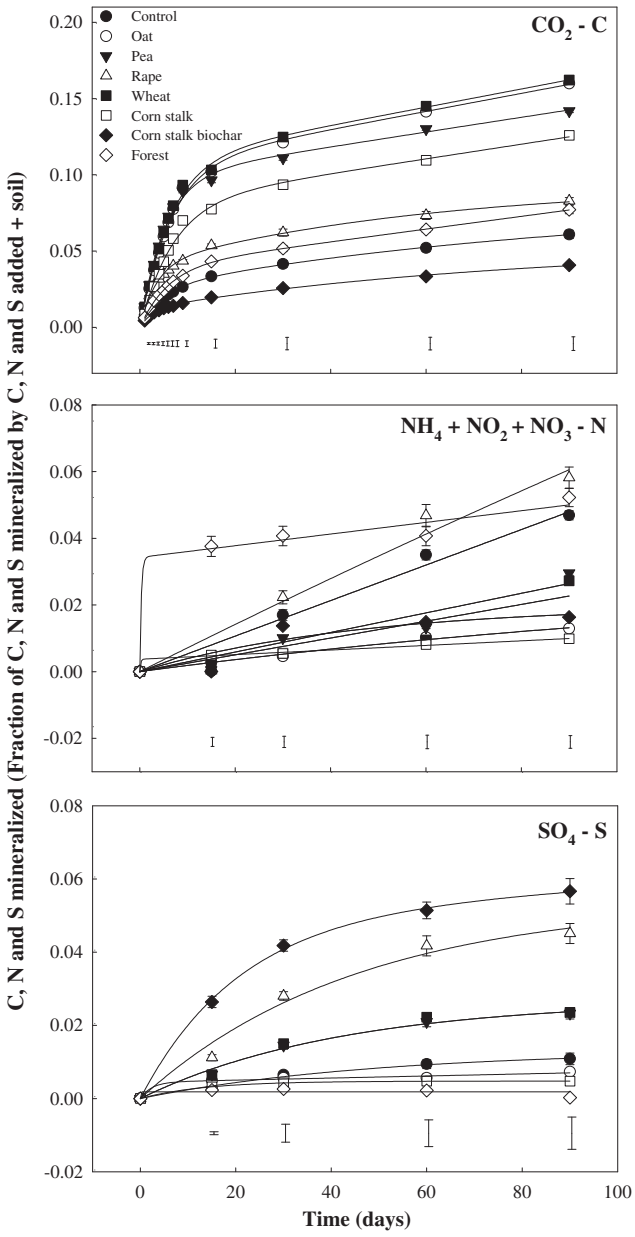

Fig. 1. Cumulative normalized amounts of CO_2, N (sum of NH_4^+, NO_3^- and NO_2^-) and S mineralized over a 90-day incubation of a Brazilian Oxisol amended with different plant residues and biochar (means and standard errors, n = 3). Bars represent the $LSD_{0.05}$.

Cumulative N mineralization (sum of mineralized NO_3^-, NO_2^- and NH_4^+) was influenced by organic matter additions (Fig. 1). The forest soil had the highest N mineralization, releasing mainly NH_4^+ (Supplementary Table S1) since the first leaching event (57.9% of mineralized N or 126.9 mg NH_4^+–N kg^{-1} soil). In these first 15 days of incubation, N immobilization as a result of residue addition did not occur (Fig. 1, Supplementary Table S1). During this first phase, N mineralization was positively correlated with applied C ($r = 0.93$, $p<0.05$, $n = 5$), C/N ($r = 0.98$, $p<0.01$, $n = 5$) and C/S ratios ($r = 0.93$, $p<0.05$, $n = 5$). However, after the first event of leaching, for all crop residues (except for the rape), there was a significant net immobilization of N, i.e., the total N mineralization in the soil amended with crop residue was less than in the control soil (Fig. 1). Higher immobilization was found in the treatments that received corn stalk, wheat and oat due to their higher C/N and C/S ratios (Table 2) as revealed by Pearson correlations. At days 30 to 90, the N immobilization shown by all but rape

Table 3
Pool sizes (X) and decay rates (k) of soil C, N and S mineralization using a double-exponential model, whereby the subscripts 1 and 2 refer to the modeled labile and stable fraction, respectively.

Treatment	X_1	X_2	k_1 (day^{-1})	k_2 (day^{-1})	R^2
C mineralization					
Control	0.0309	0.9691	0.1700	0.0004	0.9987
Forest	0.0391	0.9609	0.1701	0.0004	0.9997
Oat	0.1056	0.8944	0.1548	0.0007	0.9959
Pea	0.0985	0.9015	0.1900	0.0006	0.9948
Rape	0.0487	0.9513	0.2297	0.0004	0.9954
Wheat	0.1056	0.8944	0.1548	0.0007	0.9960
Corn stalk	0.0813	0.9187	0.1435	0.0005	0.9940
Corn stalk biochar	0.0163	0.9837	0.2326	0.0003	0.9960
N mineralization					
Control	0.0000	1.0000	0.1338	0.0005	0.9624
Forest	0.0343	0.9657	1.4582	0.0002	0.8118
Oat	0.0008	0.9992	0.1465	0.0001	0.9780
Pea	0.0000	1.0000	0.1815	0.0003	0.9274
Rape	0.0343	0.9657	1.5091	0.0002	0.8118
Wheat	0.0000	1.0000	0.1451	0.0003	0.8101
Corn stalk	0.0037	0.9963	0.2753	0.0001	0.9851
Corn stalk biochar	0.0199	0.9801	0.0218	0.0000	0.7552
S mineralization					
Control	0.0131	0.9869	0.0202	0.0000	0.9807
Forest	0.0018	0.9982	1.4600	0.0000	0.0812
Oat	0.0047	0.9953	0.2043	0.0000	0.8202
Pea	0.0212	0.9788	0.0294	0.0000	0.9829
Rape	0.0540	0.9460	0.0221	0.0000	0.9700
Wheat	0.0270	0.9730	0.0252	0.0000	0.9752
Corn stalk	0.0042	0.9958	0.0895	0.0000	0.9794
Corn stalk biochar	0.0503	0.9497	0.0484	0.0001	0.9963

residues may indicate that there was a need for external sources of N to decompose C-rich residues (in this case consuming the native soil N). Cumulative N mineralization at 90 days showed a negative correlation with the total C applied ($r=-0.82$, $p<0.05$, $n=6$), C/N ($r=-0.80$, $p<0.05$, $n=6$) and C/S ratios ($r=-0.82$, $p<0.05$; $n=6$). For most of the organic residues N mineralization was modeled with only one pool (Table 3). Rape, however, showed a large labile pool of mineralizable N, associated with its low C/N ratio. Corn stalk biochar proved to contain recalcitrant N indicated by small values of k_2 (Table 3).

Inorganic S contents in soil solution gradually increased during incubation, with high mineral S found during the initial leaching event (Fig. 1, Supplementary Table S1). Despite the fact that the forest soil had a similar C/S ratio (Table 1) compared to the agricultural area, the amount of S mineralized by the forest site was lower than that by the agricultural area ($p<0.05$) at the four events of leaching (Fig. 1). Between the soils that received plant residue additions, the highest amount of S extracted by 1 M $CaCl_2$ was found after the application of rape (which mineralized ca. 40% of the S added in 90 days), followed by pea and wheat (Fig. 1). Even greater amounts, however, were obtained from soils amended with the corn biochar (Fig. 1), despite its similar C/S ratio to the unpyrolyzed corn. The double exponential model described S release well, showing very high coefficients of correlation (Table 3), except for the soil from the forest site. Associated with high S leaching, rape and biochar showed the highest labile S fractions followed by wheat and pea.

Significant and strong relationships between cumulative C, N and S mineralization were found at the end of the incubation (90 days), mainly when only the plant residues were included in the analysis (Supplementary Fig. S2). Cumulative CO_2 evolution and N mineralization were negatively correlated. This was related to the quality of residues, whereby wide C/N plant materials caused larger CO_2 evolution than high quality plant residues (with low C/N ratios), the former also causing N immobilization. Cumulative N and S mineralization were positively correlated with each other when only plant residues were considered (Supplementary Fig. S2). A different behavior was observed between C and S mineralization, where inclusion of biochar in the analysis even improved the correlation.

3.2. S forms in residues

Although all the amendments were added on the basis of their S contents (38 g S kg^{-1} soil), we observed clear differences in S mineralization between added organic materials (Fig. 1). To examine the forms of S in the starting material (plants and biochar) we employed X-ray Absorption Near-Edge Structure (XANES) spectroscopy. The baseline-corrected and normalized experimental S K-edge XANES spectra of the plants and the biochar were characterized by the presence of three prominent absorption edge and post-edge bands in the energy ranges of 2471 to 2476, 2476 to 2479 and 2479 to 2486 eV (Fig. 2). The qualitative features of the XANES spectra indicated larger peaks in the most oxidized S state (as inorganic sulfate and ester-S) for rape and wheat, while pea, black oat and corn stalks showed significant proportions of S in the most reduced and intermediate states. The deconvolution data confirmed this information (Table 4).

Most of the S (more than 75%) present in the plant residues was C-bonded S. The spectrum obtained from corn stalks had a large background due to the low amount of total S present in the sample (Table 2). S mineralized at 15 and 30 days after the start of the incubation was correlated with the most oxidized S species obtained by XANES (Table 5).

3.3. Transformations in S pools

The net changes in the main S fractions (C-bonded S and ester-S) were evaluated at the end of the experiment (90 days) and at three days of incubation (Fig. 3). Net increases in inorganic S were observed from T_0 (without the addition of organic amendments) to T_3 in almost all treatments, except for the plots that had received additions of pea residues.

Associated with increases in inorganic S, contents of ester-S also increased (on average 40%) during the first three days of the

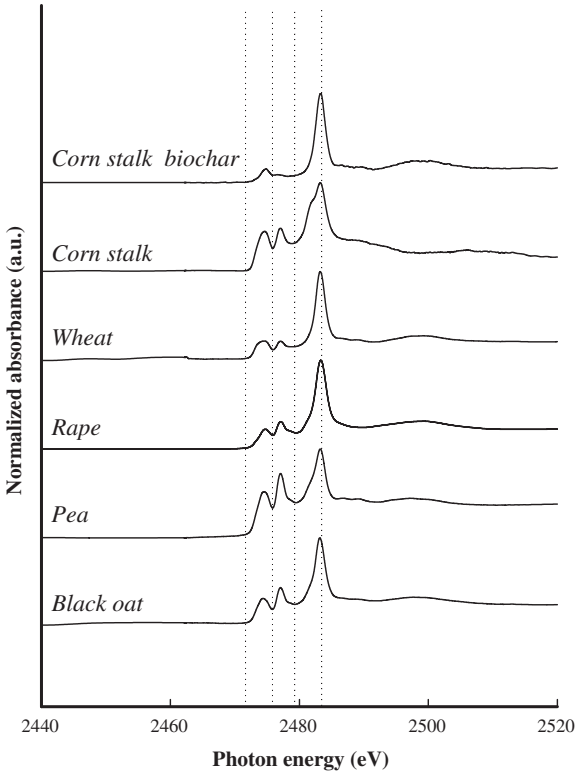

Fig. 2. Sulfur K-edge XANES spectra of the plant residues and biochar utilized in the incubation.

Table 4
Forms of S in the starting materials used in the incubation determined by XANES spectroscopy and amount of sulfate extracted at 1 h after the incubation.

S compounds	Percent of S species					$Ca(H_2PO_4)_2$ extractable S (mg kg^{-1})
	Sulfide	Thiophene	Sulfoxide	Sulfonate	Sulfate (inorganic and ester-S)	
Gaussian curve	G1	G2	G3	G4	G5	
Control	–	–	–	–	–	7.23 ± 0.33
Forest	–	–	–	–	–	11.82 ± 0.28
Oat	21.52	10.44	19.33	30.99	17.82	14.61 ± 1.35
Pea	13.43	25.78	22.35	21.51	16.96	12.48 ± 0.16
Rape	21.32	12.50	15.13	32.27	18.78	21.18 ± 0.57
Wheat	13.50	20.44	12.58	28.87	24.61	21.51 ± 2.21
Corn stalk	5.47	17.02	10.34	48.39	18.77	13.79 ± 1.03
Corn stalk biochar	13.62	12.33	3.8	26.35	43.90	19.70 ± 0.28

incubation. In most cases, the increase in ester-S was of the same magnitude as the increase in inorganic sulfate, extracted by calcium phosphate, and was accompanied by decreases in C-bonded S (Fig. 3). In contrast, by 90 days of incubation the results were variable with few discernible trends except an increase in inorganic S (Fig. 3).

4. Discussions

The results of this study showed that S forms in the plant tissues play an important role in controlling S mineralization. In residues containing highly oxidized S, the process of S mineralization was mostly governed by the enzymatic hydrolysis of the ester-S rather than the need of C to provide energy to the microorganisms. However, with the application of residues rich in C-bonded S, biological mineralization was dominant.

4.1. Relationship of S mineralization to C and N mineralization

As observed in previous studies, mineralization of C and N are more closely related than of S, thus supporting the concept of a dual mechanism system for S (McGill and Cole, 1981). In our study, we observed a clear distinction between biochar and plant materials added as organic substrates in the release of CO_2, inorganic N and SO_4^{2-}. When considering only the plant materials, cumulative CO_2 evolution and C added and the C/S ratios were closely related ($R^2 = 0.99$, $p < 0.01$, $n = 5$). These results indicate that under our experimental conditions the decomposition of C was influenced by S supply for new microbial synthesis, as reported previously by Saggar et al. (1981). When the biochar was included in the analysis, no significant relationship was observed. Despite its high recalcitrance in C mineralization, biochar had the highest amount of leached S since the first leaching event (at 15 days) (Fig. 1). During this initial stage of the mineralization experiment, S was released from the biochar as inorganic sulfate indicated by the high contents of the most oxidized S species (Fig. 2), while in the plant materials, the primary need for carbon by the micro biota or the activity of enzymes external to the cell membrane were responsible for S mineralization.

Since it is primarily the need for C rather than the need for N that causes N mineralization (McGill and Cole, 1981), the inorganic N leached at day 15 was the one present in the most labile fractions of organic C from the added plant materials (Janzen and Kucey, 1988; Singh et al., 2006; Wang et al., 2004). The inorganic N per unit soil N produced with the application of biochar (Fig. 1) was higher than the one obtained by the application of corn stalk, despite their similar C/N and C/S ratios. The lower N immobilization (Fig. 1) by corn stalk biochar than the non-charred material was due to the lower decomposition of

Table 5
Pearson correlation coefficients between S species in starting materials and mineralized S (n = 6).

	$Ca(H_2PO_4)_2$ extractable S[a]	Mineralized S at 15 days	Mineralized S at 30 days	Mineralized S at 60 days	Mineralized S at 90 days
Sulfide	0.32 ns	0.10 ns	0.21 ns	0.25 ns	0.27 ns
Thiophene	−0.33 ns	−0.36 ns	−0.27 ns	−0.21 ns	−0.22 ns
Sulfoxide	−0.51 ns	−0.68 ns	−0.57 ns	−0.49 ns	−0.49 ns
Sulfonate	−0.16 ns	−0.39 ns	−0.45 ns	−0.47 ns	−0.49 ns
Sulfate[b]	0.47 ns	**0.92****	**0.80***	0.70 ns	0.71 ns

[a] Extracted 1 h after the incubation.
[b] Ester sulfate and inorganic sulfate.
* Significant at $p < 0.05$.
** Significant at $p < 0.01$.

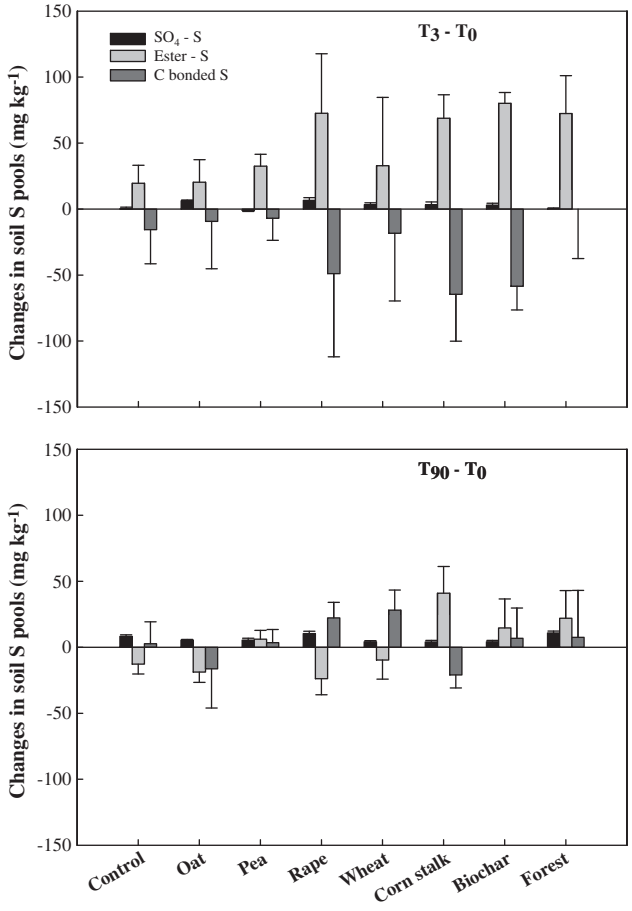

Fig. 3. Effect of added organic substrates on changes in S pools (obtained from wet-chemical fractionation) of soils at 3 and 90 days of the incubation (time-0 assessment were done before organic amendments were added).

the biochar (Fig. 1), where less native soil N was needed for maintaining soil microbial activity. High cumulative N leaching by rape residues mostly in the form of nitrate (Supplementary Table S1) after the second sampling was due to their low C/N and C/S ratios, showing no need for external sources of N such as soil N for the utilization of C by the microbes (Fig. 1). For those residues with higher C/N and C/S ratios, a longer incubation period (>6 months) may be required to assess the timing of release of immobilized N in the soils (Singh et al., 2006).

4.2. Dependency of S mineralization on S forms in residues

Effects of the added substrates on the magnitude of S mineralization were strongly influenced by the S forms of the residues (Figs. 1 and 2; Table 5), rather than by initial S tissue concentration as suggested in other studies (Janzen and Kucey, 1988; Niknahad-Gharmakher et al., 2012; Singh et al., 2006; Wu et al., 1993) that did not control for different amounts of S added. The XANES spectra of plant residues and biochar (Fig. 2) showed that much of the tissue S in these materials existed in soluble inorganic sulfate and readily degradable organic-S forms (S in amino-acids), agreeing with what was previously hypothesized (Janzen and Kucey, 1988; Singh et al., 2006).

The high proportions of highly oxidized S in wheat, rape and biochar coincided with the greatest amounts of the $CaCl_2$-extractable S after the incorporation of the plant residues and biochar to the soil (Table 5). This S was very labile and was released to a great extent during the first leaching event (Fig. 1c, Table 5), possibly indicating inorganic sulfate and very labile ester-S.

Sulfur is essential to the plant's metabolism being a constituent of the amino acids cysteine and methionine from which plant protein is synthesized. Plants absorb S mostly as sulfate (Kertesz and Mirleau, 2004) by the roots, and it is transported to the leaves where several steps of enzymatic reduction occurs for the production of cysteine, the primary S-containing amino acid in plants. Excess of absorbed sulfate can be stored as free sulfate ions (Ernst, 1998) and ester-S, like the sulfated thioglycosides ($N–O–SO_3^-$) in cruciferous plants (Fitzgerald, 1976). Plant residues had 48.4% of S in intermediate oxidation states and 32.3% in highly reduced oxidation states, while Jalilehvand (2006) measuring intact magnolia leaves found 48% of S in highly reduced states and only 15% in intermediate states. Those differences may be due to not only the plant composition itself, but also due to post treatments adopted in this study, measuring aboveground biomass after drying and grinding. Most of the difference was found in the sulfonate fraction (24.3%) showing the importance of this fraction as a reservoir of S as pointed out previously by other authors (Autry and Fitzgerald, 1990; De Bona and Monteiro, 2010). However, in our study we verified that in the short term, the most oxidized S species are responsible for supplying soil inorganic S (Table 5).

4.3. Sulfur forms in corn biochar

In this experiment, only one type of char was investigated (corn stalk biochar produced at 450 °C). Comparison of the spectra recorded from corn stalk (not charred) and biochar made from corn stalk (Fig. 2), as well as the results presented in Table 5, indicate a reduction in the sulfoxide (G3) and sulfonate (G4) peaks with the pyrolysis and an increase in the highly oxidized S species (G5) following charring of corn stalks. To the best of our knowledge no detailed studies using XANES were performed on biochar to date. Most of the available information about the S species determined by XANES in pyrogenic compounds comes from the investigation of the chemical nature of S in fossil fuels, like coals (Huffman et al., 1991; Qu et al., 2010; Sugawara et al., 2001; Wijaya and Zhang, 2012) and kerogens (Kelemen et al., 2012) which have five up to 140 times greater S contents (Huffman et al., 1991) than the plant residues used in this experiment. Equally different are the forms of S whereby the proportion of highly reduced S is higher in fossil fuels than in plant materials (Kelemen et al., 2012; Sugawara et al., 2001; Wijaya and Zhang, 2012), and more than 65% of S species consist of sulfide and thiophene-S forms (Huffman et al., 1991) especially because pyrite is found in some materials (Kelemen et al., 2012; Sugawara et al., 2001). However, the available information about sulfur compositional chemistry changes during pyrolysis of plant biomass for bioenergy (Khalil et al., 2008; Knudsen et al., 2004; Wang et al., 2010) indicate that the organically bound S has a low thermal stability, which will result in thermal decomposition following exposure to low temperatures (<450 °C) (Khalil et al., 2008; Knudsen et al., 2004), promoting the emission of S species as COS and H_2S. The transformation of inorganic sulfate, however, only occurs at higher pyrolysis temperatures, ca. 950 °C (Wang et al., 2010), emitting SO_2. Knudsen et al. (2004) conducted a detailed study on thermal decomposition of S species during combustion (up to 1100 °C) of wheat straw, which was mostly dominated by inorganic sulfate (between 40 and 50% of total S in straw) showing the decomposition of organic S species (starting at 200 °C) and the high stability of sulfate and its concentration in char as inorganic sulfate. Our results indicated that during the pyrolysis of the corn stalks at 450 °C, most of the S bonded to C (especially from sulfonates) was thermally decomposed, while ester-S and to a small extent inorganic sulfate accumulated in the final (charred) material (Table 4). The ester-S is the organic S form that was then very rapidly converted to inorganic sulfate. These results explain the higher initial release of inorganic sulfate by the application of the biochar to soil, even though it was added in the same amount of total sulfur as the plant residues.

4.4. Mechanisms of S release from residues

The increases in ester sulfate observed during the first three days of incubation (Fig. 3) agree with several authors who have also observed increases in ester-S during the initial stages of residue decomposition in soil (Freney et al., 1975; Ghani et al., 1992, 1993; Saggar et al., 1981). In addition, the periodic leaching employed in this study had stimulated the enzymatic hydrolysis of ester-S by removing excess sulfate (Ghani et al., 1992). The soil microbial community is the major player in this process, and the accumulation of ester-S is related to the mechanism used by soil microbes to store S without altering the pH of their surroundings (Fitzgerald, 1976). A decrease in C-bonded sulfur was observed for most residue applications after three days of incubation, showing that in this initial phase the biological S mineralization (McGill and Cole, 1981) was dominant. This agrees with the findings of Ghani et al. (1991), Solomon et al. (2011) and Zhao et al. (2006) that these C-bonded S (organic S in reduced and intermediate states) are the main source for S mineralization. In aerobic incubations, losses of C-bonded S forms are commonly observed when microorganisms transform C-bonded S functionalities to ester-S as an intermediate product before being released as inorganic sulfate (Ghani et al., 1992; McGill and Cole, 1981; Solomon et al., 2011).

The changes in S fractions occurring up to the end of the incubation ($T_{90}–T_0$) clearly show that organic S in the soil environment is not static, but rapidly converted from one organosulfur form to another by microbial action (Kertesz and Mirleau, 2004). In general, residues with highly oxidized S species had stimulated biochemical mineralization through the hydrolysis of ester-S, causing a reduction in this fraction (Fig. 3) and agreeing with the findings of Ghani et al. (1992) that performed periodic leaching in an incubation experiment. The additions of carbon rich materials as corn stalk and oat had stimulated the microbial activity, making C-bonded S the main functionality responsible for S supply (Fig. 3). The incorporation of S into the organic pool, observed after additions of corn stalks (Fig. 3), agrees with the findings of Eriksen (1997), in which higher incorporation of S was observed in the presence of cellulose.

Using a greater temporal resolution of observation between 3 and 90 days and additional studies using XANES, we might have been able to observe clearer trends in the S transformation driven by C, N and S

additions. Nonetheless, we were able to clearly observe the importance of the decomposability of the material (Wu et al., 1993) as well as the S forms in the residue for determining S mineralization, as well. Rich ester-S organic substrates when incorporated to the soil rapidly increased the size of the available inorganic S pool (Tables 4 and 5, Fig. 1), showing that the incorporation of rape residues and biochar into soil can readily provide plant available-S and improve the S-supplying potential of the soil (Fig. 1). This is in contrast to the incorporation of plant residues having a higher C/S ratio, which may cause S immobilization by soil microorganisms. The incorporation of such plant residues may result in at least temporary S-deficiency in soil, making it advisable to compensate these reductions by S fertilizers.

5. Conclusions

Sulfur mineralization in the present investigation seems to be driven by the form of S in the starting materials, where more oxidized species played an important role for S mineralization at earlier stages of incubation (at the 15 and 30 days). These findings confirm the hypothesis that S forms rather than S concentration in the tissue plays a major role in S mineralization. Even though only one material was charred, we could show that this process fundamentally altered S functionalities mainly in intermediate states, which were thermally broken down and transformed into highly oxidized S states. These concepts would need to be verified using different feedstocks and pyrolysis temperatures and also tested in more soil types. During the first three days of incubation, an increase of soil contents of ester-S was associated with a decrease in C-bonded S. In highly oxidized S containing residues, the process of S mineralization was mostly governed by the enzymatic hydrolysis of the ester-S pool rather than the need of carbon to provide energy to the microorganisms. With the application of C-bonded S rich residues, the dominant mechanism was biological mineralization, thus liberating S as a secondary product.

Acknowledgments

The authors are grateful for the financial support by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) to S.C.B., E.F.C. and L.R.F.A. Partial support was also provided by NSF-EAR 0819689 and USDA Hatch. Akio Enders, Kelly Hanley, Michael Rutzke, Paul A. Northrup, Robert Schindelbeck, Shri Giri and Syed Khalid are acknowledged for substantial help with experimentation and analyses. The S K-edge XANES spectra were collected at the X-19A and X-15B beamlines of the NSLS, Brookhaven National Laboratory. NSLS is supported by the U.S. Department of Energy. Many thanks to Steven J. Vanek for insightful comments during the design of the experiments. We would also like to thank Julius Blum for helping in some statistical procedures and reviewing earlier versions of the manuscript. Maria Luz Cayuela is acknowledged for helpful contributions to improve this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2013.02.003.

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