Biology and Fertility of Soils (2018) 54:349–362
https://doi.org/10.1007/s00374-018-1266-9

ORIGINAL PAPER

A comparison of indexes to estimate corn S uptake and S mineralization in the field

Walter D. Carciochi[1,2] · **Nicolás Wyngaard**[1,2] · **Guillermo A. Divito**[1] · **Miguel L. Cabrera**[3] · **Nahuel I. Reussi Calvo**[1,2] · **Hernán E. Echeverría**[1]

Received: 29 May 2017 / Revised: 29 December 2017 / Accepted: 11 January 2018 / Published online: 22 January 2018

Abstract

The development of simple predictors of sulfur (S) mineralization and its correlation with field-derived data may help improving corn S availability diagnosis. The objectives of this study were (1) to compare methods to estimate soil S mineralization, (2) to develop a model to predict soil S mineralization from S mineralization indexes and edaphic variables, and (3) to predict field-grown corn S uptake (S_{uptake}) and apparent S mineralization ($S_{min\text{-}app}$) from different S mineralization indexes and edaphic-climatic variables. We evaluated 26 experimental sites where we measured edaphic variables as soil organic C (SOC), organic C in the particulate fraction (C-PF), S mineralization potential ($S_{min\text{-}10wk}$), S mineralized during a short-term (7 days) aerobic incubation + initial inorganic S ($S_{min\text{-}7d} + S_{inorg}$), and N mineralized during a short-term (7 days) anaerobic incubation (N_{an}). Additionally, 18 field experiments were carried out to quantify S_{uptake} and $S_{min\text{-}app}$. The C-PF, $S_{min\text{-}7d} + S_{inorg}$, N_{an}, and SOC were variables significantly correlated with $S_{min\text{-}10wk}$ ($r = 0.89$, 0.89, 0.88, and 0.85, respectively). We developed a simple model to predict $S_{min\text{-}10wk}$ from selected edaphic variables ($S_{min\text{-}10wk} = 0.038{*}N_{an} + 0.106{*}SOC + 0.74$; $R_a^2 = 0.87$). The $S_{min\text{-}10wk}$, C-PF, and $S_{min\text{-}7d} + S_{inorg}$ showed a liner-plateau association with S_{uptake} ($R^2 = 0.73$, 0.53, and 0.48, respectively). We modified the method to estimate $S_{min\text{-}app}$ to account for S losses ($S_{min\text{-}app\ (modified)}$) and developed a model to predict $S_{min\text{-}app\ (modified)}$ from C-PF ($S_{min\text{-}app\ (modified)} = 4.65{*}\text{C-PF} + 9.86$; $R^2 = 0.62$) or $S_{min\text{-}10wk}$ ($S_{min\text{-}app\ (modified)} = 3.0{*}S_{min\text{-}10wk} + 7.4$; $R^2 = 0.54$). Our results demonstrate that S mineralization indexes can be used to predict corn S availability under field conditions.

Keywords Incubations · Sulfur balance · Apparent S mineralization · Field trials

Introduction

Sulfur (S) deficiencies in crops have become a worldwide problem in recent years (Eriksen 2009), and there is limited information on designing S fertilization plans as compared with other nutrients like nitrogen (N) and phosphorus (P). Soil sulfate concentration (SO_4^{-2}-S) at sowing ($S_{initial}$) has been broadly used with varied success to predict S availability to crops (Van Biljon et al. 2004; Pagani and Echeverría 2011; Carciochi et al. 2016). These contrasting results can be partially explained by the unaccounted contribution of S through mineralization during the growing season (Eriksen et al. 1995).

Different methods have been proposed to study S mineralization. The long-term (≥ 10 weeks) aerobic incubation technique is considered the standard method to determine the S mineralization potential (S_0). Although this technique has been widely used in many studies (Pirela and Tabatabai 1988; Ghani et al. 1991; Saviozzi et al. 2006; Boye et al. 2009), it is lengthy and laborious, and therefore unsuitable for soil testing laboratories. The use of a short-term (7 days) aerobic incubation ($S_{min\text{-}7d}$) has been proposed as an alternative to long-term incubations (Wyngaard and Cabrera 2015). Although $S_{min\text{-}7d}$ was highly correlated with S_0 ($r = 0.85$), this association was determined using only four soils (Wyngaard and Cabrera 2015).

✉ Walter D. Carciochi
waltercarciochi@hotmail.com

[1] Unidad Integrada Balcarce EEA INTA Balcarce-Fac. Ciencias Agrarias (UNMdP), Ruta 226 km 73.5, Balcarce, Buenos Aires, Argentina

[2] Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina

[3] Crop and Soil Sciences Department, University of Georgia, 120 Carlton St, Athens, GA, USA

Due to the close relationship between S and N microbial turnover in soil, it was suggested that S mineralization can be estimated from N mineralization (Tabatabai and Al-Khafaji 1980; Echeverría et al. 1996; Niknahad-Gharmakher et al. 2009). Among the methods to estimate N mineralization, the short-term (7 days) anaerobic incubation (N_{an}) has been widely used, as it is a fast, simple, and precise technique (Echeverria et al. 2000; Soon et al. 2007; Orcellet et al. 2017). In this regard, Wyngaard and Cabrera (2015) have proposed the use of N_{an} as a S_0 predictor, since they have found a strong relationship between both variables.

Most S in soils (> 95%) is organic (S_{org}) (Ghani et al. 1991). As S_{org} is associated with soil organic C (SOC), many studies have correlated S_{org} and/or SOC with S mineralization, observing a positive relationship (Riffaldi et al. 2006) or no relationship between these variables (Pirela and Tabatabai 1988; Eriksen et al. 1995). A possible explanation for these different results is that S mineralization does not depend on the size of the whole S organic pool (estimated by SOC or S_{org}) but on the size of the easily mineralizable fraction. The lability of soil organic matter is inversely associated with the clay content, as fine particles protect organic matter from decomposition (Schnug and Haneklaus 1998; Six et al. 2002). Consequently, the SOC/clay and S_{org}/clay ratios may improve the S mineralization estimation as compared with SOC and S_{org}, respectively. Another alternative to account for the physical protection of organic matter is the one suggested by Cambardella and Elliott (1992). These authors proposed a particle size separation of soil into two fractions: the stable fraction associated with minerals (< 53 μm) and the labile particulate fraction (PF, > 53 μm). The S content in the PF (S-PF) was related to S mineralization (Wyngaard and Cabrera 2015), but this relationship needs to be validated as it was developed with a limited number of soils. The C content in the PF (C-PF) is associated with N mineralization potential (Domínguez et al. 2016). However, it has never been evaluated as a S mineralization index. In this sense, it is interesting to evaluate C-PF as a predictor of S mineralization for its simplicity and lower cost as compared with S-PF.

Plant S uptake (S_{uptake}) is often used as a S mineralization estimation. Previous studies have related different chemical S extraction methods with S_{uptake} by plants growing in pots (Scott 1981; Bansal et al. 1983; Eriksen 1997) or in field conditions (Blair et al. 1991). However, none of these studies related S_{uptake} to S mineralization indexes.

The use of S mineralization indexes to determine S availability for crops is limited, as mineralization in the field does not only depend on the size of the mineralizable pool but on edaphic-climatic variables (texture, precipitations, temperature, among others). Thus, it is necessary to develop a model to predict S mineralization in field that considers all of these variables. The use of a simplified balance was proposed to calculate the apparent N mineralization in the field (Cabrera and Kissel 1988; Engels and Kuhlmann 1993; Egelkraut et al. 2003; Alvarez and Steinbach 2011). In the same way, the S balance method would allow calculating the apparent S mineralization ($S_{min\text{-}app}$) in unfertilized plots from the soil SO_4^{-2}-S content at sowing ($S_{initial}$) and at crops physiological maturity ($S_{residual}$), and the S_{uptake}. However, so far, there are no reports of the use of a simplified balance to quantify S mineralization in field conditions.

Many studies evaluated S mineralization under laboratory conditions using long-term aerobic incubations (Pirela and Tabatabai 1988; Ghani et al. 1991; Saviozzi et al. 2006; Boye et al. 2009). However, only a few studies aimed to estimate the results from long-term incubations using simplified S mineralization indexes or soil properties (Niknahad-Gharmakher et al. 2009; Wyngaard and Cabrera 2015). Moreover, none of these studies associated long-term incubation results, S mineralization indexes, or soil properties with S_{uptake} or $S_{min\text{-}app}$ determined under field conditions. The development of simple predictors of S mineralization and its correlation with field-derived data can help improving S fertilization diagnosis based solely in $S_{initial}$. Therefore, the objectives of this study were (1) to compare methods to estimate soil S mineralization, (2) to develop a model to predict soil S mineralization from S mineralization indexes and edaphic properties, and (3) to predict field-grown corn S_{uptake} and $S_{min\text{-}app}$ using different S mineralization indexes and edaphic-climatic variables as predictors.

Materials and methods

Soils

Twenty-six topsoil (0–20 cm) samples were taken in 2013 and 2014 from contrasting sites of the Argentinean Pampas (from 30.8° to 38.2° S and 57.1° to 61.8° W). Soil texture ranged from sandy loam to silt clay loam and SOC ranged from 10.3 to 46.1 g kg^{-1}. Mean annual rainfall at the experimental sites was between 850 and 1000 mm, and average daily mean temperature was between 14.5 and 19 °C. Further description of the experimental sites is in Table 1. Soil samples were dried at 30 °C and ground to pass a 2-mm sieve for all analysis except for total S (S_t) and SOC, when a 0.5-mm sieve was used.

Soil analyses

Soil properties

For all analytical techniques, three laboratory replications per sample were performed. The S_t determination was performed after a wet digestion with HNO_3 and $HClO_4$ (Zhao et al. 1994), and the extracted S was quantified by inductively coupled plasma emission spectrometry (ICP-AES) (Thermo

Table 1 Site location and soil characteristics (soil type, clay, and sand content, pH)

Location			Soil type (USDA)	Clay (g 100 g^{-1})	Sand (g 100 g^{-1})	pH (1:2.5 in water)
Site	Latitude	Longitude				
S1	34.0° S	61.8° W	TH[†]	18.9	46.8	6.1
S2	37.7° S	58.4° W	TA	23.6	32.5	5.9
S3	37.8° S	58.1° W	TA	26.3	23.1	6.4
S4	34.1°S	61.8° W	TH	10.3	72.9	6.1
S5	34.1°S	61.8° W	TH	14.6	60.4	6.3
S6	34.1°S	61.8° W	TH	21.2	44.1	6.4
S7	31.2° S	61.5° W	TA	25.2	3.0	6.0
S8	31.6° S	61.7° W	TA	26.2	21.5	8.4
S9	30.8° S	60.5° W	TA	29.6	2.2	5.9
S10	31.2° S	61.5° W	TA	21.0	2.9	6.1
S11	37.1° S	57.2° W	TA	19.4	41.2	5.8
S12	37.1° S	57.2° W	TA	21.7	33.8	6.0
S13	38.2° S	57.9° W	TA	19.4	33.4	5.9
S14	38.2° S	57.9° W	TA	21.9	32.4	5.9
S15	35.6° S	61.1 ° W	EH	12.5	72.1	5.9
S16	35.6° S	61.1 ° W	EH	16.9	52.0	5.8
S17	37.8° S	58.3° W	TA	21.3	44.9	6.1
S18	37.7° S	58.6° W	TA	23.9	32.8	5.8
S19	37.1° S	57.2° W	TA	19.4	34.3	6.0
S20	37.1° S	57.1° W	TA	24.5	35.5	5.8
S21	37.8° S	58.3° W	TA	23.5	40.5	5.7
S22	37.8° S	58.3° W	TA	23.5	43.0	5.5
S23	37.8° S	58.3° W	TA	25.8	39.6	5.6
S24	37.8° S	58.3° W	TA	27.0	39.0	5.6
S25	34.2° S	61.6° W	TH	16.6	49.4	5.6
S26	34.2° S	61.6° W	TH	16.6	50.5	5.4

[†] TH, typic hapludoll; TA, typic argiudoll; EH, entic hapludoll

Fisher 61E). The SO_4^{-2}-S concentration (S_{inorg}) was determined by ion chromatography on 0.01 M NH_4Cl (1:10, soil:solution ratio) extracts (Maynard et al. 1987). Organic S was calculated by subtracting S_{inorg} from S_t. To determine SOC, a wet combustion method with maintenance of the oxidation reaction temperature (120 °C) for 90 min was performed (Schlichting et al. 1995). To separate the particulate fraction (PF), soil samples were dispersed and wet-sieved through a 53-μm sieve (Cambardella and Elliott 1992). Organic C content in the particulate fraction (C-PF) was quantified as previously explained for SOC, while S in the PF (S-PF) was measured as described for S_t.

Incubations

The long-term open incubation procedure was performed as described by Pirela and Tabatabai (1988). In detail, 20 g soil were mixed with 20 g of acid-washed sand and transferred into a leaching tube with glass wool at the bottom. The soil-sand mixture was leached with 200 mL of 0.01 M $CaCl_2$ to remove the initial sulfate. Then, excess water was removed by vacuum suction at 6 kPa, and samples were covered with a porous plastic film (PARAFILM®, Menasha, WI) and incubated at 30 °C and at a water content of 80% of field capacity. Soil moisture was corrected gravimetrically every 3 days and samples were leached with 0.01 M $CaCl_2$ every 2 weeks for a 10-week period. Sulfate concentration in the leachate was measured by ion chromatography (Met Rohm IC 820 separation system, 819 conductivity detector with carbonate and cation suppression).

To describe soil S mineralization, data from the long-term open incubation technique were fitted to the following models based on previous studies (Zhou et al. 1999; Riffaldi et al. 2006; Saviozzi et al. 2006):

$$\textit{First-order model}: S_m = S_o\ (1-\exp(-k_F t))$$

$$\textit{Zero-order model}: S_m = k_Z t + \textit{intercept}$$

where S_m is the cumulative S mineralized (mg kg^{-1}) at a specific time (t) (week); S_0 is the potentially mineralizable S (mg kg^{-1}); k_F is the first-order rate constant ($week^{-1}$); and k_Z the zero-order rate constant (mg S kg^{-1} $week^{-1}$).

The S_{min-7d} determination was performed as proposed by Keeney and Bremner (1962). A 10-g soil sample was mixed with 30 g of acid-washed sand and transferred to a 50-mL plastic tube. After this, samples were moistened to 80% of field capacity water content, covered with a porous plastic film (PARAFILM®, Menasha, WI), and incubated for 7 days at 40 °C. Water content was corrected gravimetrically every 3 days. After the incubation period, SO_4^{-2}-S was extracted with 0.01 M NH_4Cl at a 10:1 solution/soil ratio (Maynard et al. 1987) and quantified by ion chromatography. To obtain the S_{min-7d}, the initial SO_4^{-2}-S concentration (S_{inorg}) was subtracted from the final value ($S_{min-7d} + S_{inorg}$).

Finally, to determine N_{an}, a short-term anaerobic incubation was performed. The NH_4^+ produced after the incubation of 10 g soil saturated with distilled water at 40 °C for 7 days (Keeney 1982) was quantified by steam micro-distillation (Bremner and Keeney 1965).

Field experiments

In 2013 and 2014, field experiments were carried out in 18 out of the 26 experimental sites. The objective of these experiments was to determine S uptake by corn aerial biomass (S_{uptake}) and the apparent S mineralization ($S_{min-app}$). Three replications were performed at each site, and the size of each plot was 12 by 5 m. Corn was sown at a 60,000 to 80,000 plant ha^{-1} density, depending on the site. All experiments were fertilized with N (200 kg N ha^{-1}) as urea (46 g N 100 g^{-1}) and P (30 kg P ha^{-1}) as triple superphosphate (20 g P 100 g^{-1}), but no S fertilizer was applied. All experiments were performed under no tillage, without irrigation, and in soils with deep groundwater tables (below rooting zone). When necessary, weeds were controlled by glyphosate [N-(phosphonomethyl)glycine] application at a 1.44 kg a.i. ha^{-1} rate. Rainfall and average daily mean temperature data during corn growing season were obtained from research meteorological stations located in or near the experimental sites.

At corn sowing and physiological maturity, composite soil samples (eight subsamples per plot) were taken at 0–20, 20–40, and 40–60 cm depths. Samples were dried at 30 °C and ground to pass a 2-mm sieve. Soil SO_4^{-2}-S concentration was determined as described in the soil analysis section. The bulk density of each site, estimated as proposed by Hollis et al. (2012), was used to convert SO_4^{-2}-S concentrations from milligrams per kilogram to kilogram per hectare.

At physiological maturity, ten plants were cut at ground level and dried at 60 °C. Plant samples were weighed and ground. Plant S concentration was measured by dry combustion at 1350 °C and thermoconductivity detection with TruSpec S analyzer (LECO, St. Joseph,MI, USA). Plant density was determined in each site to calculate S_{uptake} (kg S ha^{-1}).

The simplified balance method applied for N by Alvarez and Steinbach (2011) was used to determine the apparent S mineralization ($S_{min-app}$):

$$S_{\text{min-app}} = S_{uptake} + S_{residual} - S_{initial}$$

where $S_{min-app}$ (kg ha^{-1}) represents the difference between net S mineralization and S losses from soil-plant system; S_{uptake} the amount of S (kg ha^{-1}) accumulated in corn aerial biomass at physiological maturity; $S_{residual}$ and $S_{initial}$ the SO_4^{-2}-S content (kg ha^{-1}) in soil at 0–60 cm depth in physiological maturity and sowing, respectively.

As $S_{min-app}$ does not consider S losses, we aimed to improve the S field balance by accounting for this last process. To do so, we weighted $S_{initial}$ by an uptake efficiency factor analogous to the one used in field N balances (Meisinger 1984). We used uptake efficiency values described for N, as there are no reports of $S_{initial}$ efficiency in literature. For N, initial NO_3^- uptake efficiency is described to range between 35 and 70% depending on precipitations (Meisinger et al. 2008). As S leaching ($S_{leaching}$) is the main process by which $S_{initial}$ is lost from the system (Schoenau and Malhi 2008), we considered rainfall from sowing to V_6 stage when assigning an uptake efficiency to each site: a 35% S uptake efficiency was assigned to the site with greater rainfall (141 mm), while a 70% value was assigned to the site with lower rainfall (5 mm). A $S_{initial}$ uptake efficiency between 35 and 70% proportional to the precipitations between sowing and V_6 was assigned to the rest of the sites. We named this new balance $S_{min-app\ (modified)}$:

$$S_{\text{min-app }(modified)} = S_{uptake} + S_{residual} - S_{initial}{}^{*}\ Uptake\ efficiency$$

Statistical analysis

Zero- and first-order models for S mineralization were fitted using the R software (R Core Team 2017). Difference between sites for some variables was analyzed using the ANOVA procedure included in the R software (R Core Team 2017). Significantly, different means were compared using a LSD test at $p = 0.05$. Correlations between some variables were determined using the cor.test procedure included in the R software (R Core Team 2017). The stepwise selection method, included in the R software, was used to determine the best variables combinations to explain $S_{min-10wk}$, $S_{min-app}$, and $S_{min-app\ (modified)}$ using a maximum p value of 0.05. Linear models to predict $S_{min-app}$ and $S_{min-app\ (modified)}$ were fitted using the lm procedure included in the R software (R Core Team 2017). The relationship between S_{uptake} and some variables was described with linear-plateau models: $y = a + b * x$ if $x \leq c$ and $y = a + b * c$ if $x > c$, where a is the intercept, b is the slope during the linear phase, and c is the value of x at which the linear model reaches a plateau.

Results and discussion

Soil properties and S mineralization indexes

Some soil characteristics and S mineralization indexes are shown in Table 2. Total S content (S_t) was 487 ± 157 mg kg^{-1} and organic S (S_{org}) was in average a 98.6% of S_t. Similar values of S_t were reported by Tabatabai and Al-Khafaji (1980), Boye et al. (2009), and Niknahad-Gharmakher et al. (2009) for arable soils from Iowa, Sweden, and France, respectively, where SOC content was similar to that in our study (between 10.3 and 46.1 g kg^{-1}). The SOC/S_{org} ratios ranged from 28.6 to 75 and are within the reported range (Pirela and Tabatabai 1988; Riffaldi et al. 2006; Niknahad-Gharmakher et al. 2009). Organic C in the PF and S-PF ranged around 3.2 g kg^{-1} and 97.2 mg kg^{-1} in average, respectively.

The $S_{min\text{-}7d}$ ranged from 0.2 to 3 mg kg^{-1}. When the initial inorganic S was not subtracted, ($S_{min\text{-}7d} + S_{inorg}$) ranged from 1.3 to 10 mg kg^{-1}. In average, $S_{min\text{-}7d}$ represented 0.2% of S_{org}, while $S_{min\text{-}10wk}$ represented 1.1%. We observed a great variability between laboratory replications in the $S_{min\text{-}7d}$ technique (avg. 56.3%; Table 2). This great variability is probably a consequence of the difficulty of adjusting contrasting samples to a water content of 80% of field capacity. The N_{an} ranged between 19.3 and 159.6 mg kg^{-1}, and this range is within the one reported for agricultural soils in the same area by Reussi Calvo et al. (2013) and Orcellet et al. (2017).

Long-term S mineralization incubation

Mineralizable S determined by long-term (10 weeks) aerobic incubation ($S_{min\text{-}10wk}$) ranged between 2.2 and 12.8 mg kg^{-1} (Table 3). These values were in line with those determined in similar soils from Argentina (Echeverría et al. 1996), and in other soils from Chile (Pirela and Tabatabai 1988), France (Niknahad-Gharmakher et al. 2009), and the USA (Wyngaard and Cabrera 2015).

To describe S mineralization kinetics, zero- and first-order models were fitted. The R^2 values were high for both models, ranging from 0.93 to 0.99 for zero-order models and from 0.95 to 1.00 for first-order models (Table 3). Although the first-order model fits well for all the soils, the resulting S_0 values were very high (> 92 mg kg^{-1}) and unrealistic for 8 out of 26 soils where the zero-order model fitted better. In these eight soils, S_0 represents between 25 and 97% of S_t, whereas this value is generally described to be lower than 15% (Pirela and Tabatabai 1988; Saviozzi et al. 2006; Wyngaard and Cabrera 2015). Similar results were reported by Pirela and Tabatabai (1988), Tabatabai and Chae (1991) and Zhou et al. (1999) who could not fit the first-order model or obtained unrealistic S_0 values for some of the studied soils. Examples of these contrasting relationships between cumulative S mineralized and incubation time are shown in Fig. 1. For some soils, the rate of S release decreased with time, showing a curvilinear relationship (Fig. 1a), while in other soils this relationship was linear (Fig. 1b). Similar results were reported by Pirela and Tabatabai (1988) and Saviozzi et al. (2006), who observed that some soils presented a linear fit while others presented a quadratic fit. This may be a consequence of the different size of the easily mineralizable pool between soils: soils with a greater labile pool producing a mineralization flush during the first incubation weeks which results in a quadratic fit (Saviozzi et al. 2006). Meanwhile, Tabatabai and Al-Khafaji (1980) and Boye et al. (2009) described that cumulative amounts of S mineralized were linear with time, while other authors reported a decreasing rate of S release over time (Echeverría et al. 1996; Zhou et al. 1999; Saviozzi et al. 2006).

The first-order rate constant k_F varied between 0.008 and 0.197 $week^{-1}$ without considering the eight soils with a high S_0, where the k_F was lower than 0.004 $week^{-1}$ (Table 3). Similar rates of mineralization k_F were also reported by Pirela and Tabatabai (1988), Tabatabai and Chae (1991), and Zhou et al. (1999), but our results are lower than those reported by Riffaldi et al. (2006) and Saviozzi et al. (2006). The product of S_0 and k_F (S_0k_F), which is called the initial potential rate of S mineralization, was used by Riffaldi et al. (2006) and Saviozzi et al. (2006) to estimate S mineralization. This product is described to be a better predictor of S mineralization than S_0 and k_F, as it considers the interdependence between these two variables. In our study, high S_0 values result from low k_F values. Therefore, the product between these two variables would help fixing the problem of great S_0 values.

For the zero-order model, the slope k_Z varied between 0.23 and 1.12 mg S kg^{-1} $week^{-1}$ (Table 3). Our results were similar to those reported by Niknahad-Gharmakher et al. (2009) and Pirela and Tabatabai (1988) for agricultural soils, but were lower than those reported by Tabatabai and Al-Khafaji (1980), who reported an average k_Z value of 2.5 mg kg^{-1} $week^{-1}$ for pasture soils.

Correlation between S mineralization indexes

Table 4 shows the Pearson correlation coefficients (r) between different S mineralization indexes. The S_0 estimated from first-order models was not correlated with any of the analyzed variables. This is due to the lack of fit of the data to a first-order model in some soils. For these data points, a zero-order model fitted better (Table 3). Moreover, k_Z correlated better with $S_{min\text{-}10wk}$ than k_F did ($r = 1$ vs. $r = 0.8$, Table 4), indicating that S mineralization kinetics in the soils we analyzed evolved predominantly linear with time. Because of this, we decided to use $S_{min\text{-}10wk}$ as a reference S mineralization capacity value instead of S_0. Although S_0 was not related with $S_{min\text{-}10wk}$, the S_0k_F product was highly correlated with $S_{min\text{-}10wk}$ ($r = 0.93$). This finding contradicts the results from Riffaldi et al. (2006) and Saviozzi et al. (2006), who did not find

Table 2 Some soil properties and S mineralization indexes (mean ± SD; $n = 3$)

Site	S_t (mg kg^{-1})	S_{inorg} (mg kg^{-1})	S_{org} (mg kg^{-1})	S_{org}/clay	SOC (g kg^{-1})	SOC/clay	SOC/S_{org}	C-PF (g kg^{-1})	S-PF (mg kg^{-1})	$S_{min\text{-}7d}$ (mg kg^{-1})	$S_{min\text{-}7d} + S_{inorg}$ (mg kg^{-1})	N_{an} (mg kg^{-1})
S1	404 ± 16	2.4 ± 0.1	400 ± 16	21.2 ± 0.9	14.0 ± 0.4	0.7 ± 0.0	35.1 ± 0.9	1.3 ± 0.6	103.1 ± 2.3	0.6 ± 0.2	3.0 ± 0.2	36.7 ± 1.1
S2	449 ± 35	4.6 ± 0.1	440 ± 35	18.6 ± 1.5	28.0 ± 1.7	1.2 ± 0.1	63.5 ± 3.8	2.4 ± 0.4	77.7 ± 0.5	0.9 ± 0.2	5.6 ± 0.2	46.3 ± 0.0
S3	621 ± 49	4.3 ± 0.2	613 ± 49	23.3 ± 1.9	31.6 ± 1.0	1.2 ± 0.0	51.5 ± 1.7	2.6 ± 0.2	59.2 ± 6.8	1.2 ± 0.2	5.5 ± 0.2	60.9 ± 2.5
S4	363 ± 23	1.8 ± 0.4	359 ± 23	34.9 ± 2.2	10.6 ± 1.1	1.0 ± 0.1	29.4 ± 3.0	2.3 ± 0.6	190.3 ± 2.5	0.8 ± 0.4	2.6 ± 0.4	25.4 ± 1.5
S5	372 ± 29	3.0 ± 0.2	366 ± 29	25.1 ± 2.0	13.8 ± 0.8	0.9 ± 0.1	37.6 ± 2.3	2.4 ± 0.6	142.9 ± 7.9	0.2 ± 0.0	3.2 ± 0.0	30.6 ± 1.9
S6	444 ± 40	2.9 ± 0.2	438 ± 40	20.7 ± 1.9	19.0 ± 0.6	0.9 ± 0.0	43.4 ± 1.3	2.4 ± 0.5	107.4 ± 7.2	0.9 ± 0.1	3.8 ± 0.1	48.4 ± 1.7
S7	411 ± 33	2.6 ± 0.4	406 ± 33	16.1 ± 1.3	12.2 ± 0.0	0.5 ± 0.0	30.1 ± 0.1	1.7 ± 0.2	18.0 ± 0.5	0.4 ± 0.5	3.0 ± 0.5	38.5 ± 1.9
S8	412 ± 20	5.6 ± 0.2	402 ± 20	15.4 ± 0.8	30.2 ± 0.6	1.2 ± 0.0	75.0 ± 1.5	5.2 ± 0.2	62.1 ± 6.6	3.0 ± 0.6	8.5 ± 0.6	136.5 ± 4.3
S9	376 ± 14	3.7 ± 0.2	370 ± 14	12.5 ± 0.5	15.2 ± 0.3	0.5 ± 0.0	41.1 ± 0.8	1.8 ± 0.1	16.0 ± 1.3	0.8 ± 0.8	4.5 ± 0.8	41.1 ± 2.3
S10	385 ± 23	4.3 ± 0.4	377 ± 23	18.0 ± 1.1	16.0 ± 0.7	0.8 ± 0.0	42.5 ± 1.8	3.6 ± 0.1	34.1 ± 6.6	1.3 ± 0.5	5.6 ± 0.5	73.4 ± 2.6
S11	566 ± 22	5.1 ± 0.1	557 ± 22	28.7 ± 1.1	32.9 ± 0.7	1.7 ± 0.0	59.1 ± 1.3	5.5 ± 0.3	96.3 ± 7.1	1.3 ± 1.2	6.4 ± 1.2	54.4 ± 1.4
S12	603 ± 48	4.1 ± 0.1	596 ± 48	27.5 ± 2.2	33.2 ± 1.1	1.5 ± 0.1	55.8 ± 1.9	5.3 ± 0.1	81.3 ± 3.4	1.5 ± 0.1	5.6 ± 0.1	51.9 ± 2.2
S13	571 ± 22	3.8 ± 0.0	564 ± 22	29.0 ± 1.1	32.1 ± 1.6	1.6 ± 0.1	56.8 ± 2.8	3.5 ± 0.2	89.1 ± 15.6	1.7 ± 0.5	5.5 ± 0.5	62.8 ± 7.1
S14	672 ± 4	4.7 ± 0.0	664 ± 4	30.3 ± 0.2	38.0 ± 1.5	1.7 ± 0.1	57.2 ± 2.3	4.2 ± 0.2	87.8 ± 0.7	1.4 ± 0.5	6.0 ± 0.5	83.6 ± 2.8
S15	362 ± 51	2.0 ± 0.1	358 ± 51	28.7 ± 2.3	10.3 ± 1.2	0.8 ± 0.1	28.6 ± 3.3	1.2 ± 0.3	176.7 ± 1.9	0.8 ± 0.9	2.8 ± 0.9	19.3 ± 4.2
S16	446 ± 31	3.0 ± 0.1	440 ± 31	26.1 ± 2.5	18.3 ± 0.8	1.1 ± 0.1	41.5 ± 1.8	1.6 ± 0.7	126.9 ± 7.8	1.0 ± 0.5	4.0 ± 0.5	39.3 ± 2.0
S17	417 ± 51	1.3 ± 0.1	413 ± 51	19.4 ± 3.0	22.2 ± 0.8	1.0 ± 0.0	53.7 ± 2.0	1.5 ± 0.4	102.1 ± 1.4	1.0 ± 0.3	2.4 ± 0.3	31.5 ± 2.1
S18	552 ± 52	4.3 ± 0.3	546 ± 52	22.8 ± 2.4	35.2 ± 0.1	1.5 ± 0.0	64.6 ± 0.1	2.6 ± 0.4	73.8 ± 3.0	0.5 ± 1.0	4.7 ± 1.0	63.0 ± 1.8
S19	511 ± 8	5.6 ± 0.1	501 ± 8	25.8 ± 0.3	30.9 ± 0.3	1.6 ± 0.0	61.7 ± 0.6	5.7 ± 0.3	88.2 ± 3.4	1.4 ± 0.7	7.0 ± 0.7	88.3 ± 3.5
S20	677 ± 12	7.7 ± 0.6	663 ± 12	27.0 ± 0.5	46.1 ± 0.5	1.9 ± 0.0	69.6 ± 0.8	12.3 ± 0.5	150.8 ± 16.5	2.3 ± 0.8	10.0 ± 0.8	159.6 ± 19.6
S21	588 ± 45	3.2 ± 0.3	582 ± 45	24.7 ± 1.9	26.9 ± 0.4	1.1 ± 0.0	46.3 ± 0.7	2.6 ± 0.3	96.3 ± 4.8	0.7 ± 0.4	4.0 ± 0.4	41.3 ± 2.7
S22	482 ± 94	4.7 ± 0.3	473 ± 94	20.1 ± 4.0	27.4 ± 0.7	1.2 ± 0.0	57.9 ± 1.5	3.3 ± 0.3	108.9 ± 2.5	0.4 ± 0.6	5.1 ± 0.6	43.2 ± 0.4
S23	615 ± 15	3.9 ± 0.3	608 ± 15	23.6 ± 0.6	28.5 ± 0.1	1.1 ± 0.0	46.8 ± 0.2	3.3 ± 0.3	103.7 ± 5.3	0.6 ± 0.4	4.5 ± 0.4	44.1 ± 0.8
S24	576 ± 15	2.6 ± 0.2	571 ± 15	21.2 ± 0.6	28.5 ± 1.8	1.1 ± 0.1	49.8 ± 3.1	2.8 ± 0.3	91.5 ± 1.8	1.9 ± 0.3	4.4 ± 0.3	42.9 ± 2.1
S25	381 ± 6	1.1 ± 0.2	378 ± 6	22.7 ± 0.4	11.4 ± 0.5	0.7 ± 0.0	30.1 ± 1.2	1.4 ± 0.3	121.9 ± 0.8	0.2 ± 0.3	1.3 ± 0.3	24.8 ± 1.8
S26	410 ± 30	5.2 ± 0.4	402 ± 30	24.2 ± 1.8	11.9 ± 0.3	0.7 ± 0.0	29.5 ± 0.7	1.7 ± 0.5	122.0 ± 4.4	0.4 ± 0.2	5.6 ± 0.2	22.4 ± 3.1
Mean VC (%)[†]	6.4	8.0	6.4	6.4	3.5	3.5	3.5	15.6	5.5	56.3	10.9	5.3
p value	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
$LSD_{5\%}$	58.9	0.4	58.9	2.9	1.5	0.1	3.1	0.6	10.2	0.9	0.9	7.6

[†] Average variation coefficient between the 26 sites

Table 3 Parameters, determination coefficients (R^2) for first- and zero-order models and cumulative S mineralized after 10 weeks aerobic incubation ($S_{min\text{-}10wk}$) (mean ± SD; $n = 3$)

Site	First-order model				Zero-order model			$S_{min\text{-}10wk}$ (mg kg^{-1})
	S_0 (mg kg^{-1})	k_F (week^{-1})	S_0k_F (mg kg^{-1} week^{-1})	R^2	Intercept	k_z (mg kg^{-1} week^{-1})	R^2	
S1	19.0	0.023	0.45	0.993	− 0.04	0.41	0.995	4.0 ± 0.8
S2	13.1	0.059	0.78	0.999	0.26	0.58	0.992	6.0 ± 0.9
S3	9.2	0.080	0.73	0.999	0.29	0.50	0.986	5.1 ± 0.9
S4	92.7	0.004	0.36	0.999	− 0.01	0.35	0.999	3.5 ± 0.8
S5	9.9	0.048	0.47	0.996	0.13	0.37	0.992	3.8 ± 1.4
S6	16.7	0.027	0.45	0.995	0.03	0.40	0.993	3.8 ± 1.2
S7	279.9	0.001	0.40	0.997	0.01	0.39	0.998	4.0 ± 0.7
S8	329.2	0.003	0.87	0.992	− 0.29	0.90	0.996	8.7 ± 0.9
S9	357.3	0.001	0.34	0.989	− 0.11	0.36	0.991	3.5 ± 1.1
S10	38.5	0.017	0.66	1.000	0.05	0.61	0.999	6.1 ± 1.3
S11	11.2	0.113	1.27	1.000	0.61	0.75	0.975	7.6 ± 0.1
S12	11.7	0.099	1.16	0.995	0.56	0.72	0.979	7.5 ± 0.0
S13	13.0	0.080	1.04	0.992	0.49	0.70	0.985	7.4 ± 0.2
S14	10.8	0.136	1.46	0.997	0.80	0.78	0.965	8.1 ± 0.6
S15	134.9	0.002	0.24	0.971	− 0.12	0.25	0.977	2.6 ± 0.6
S16	15.5	0.025	0.38	0.994	0.07	0.34	0.993	3.4 ± 0.6
S17	104.8	0.002	0.21	0.952	−0.21	0.23	0.975	2.2 ± 0.6
S18	15.2	0.055	0.84	0.999	0.24	0.65	0.992	6.5 ± 0.5
S19	10.9	0.109	1.19	1.000	0.57	0.72	0.977	7.3 ± 0.4
S20	13.4	0.197	2.64	0.997	1.63	1.12	0.932	11.8 ± 0.3
S21	28.6	0.021	0.59	0.999	0.04	0.54	0.998	5.3 ± 0.6
S22	27.1	0.018	0.47	0.997	0.09	0.43	0.997	4.4 ± 0.8
S23	23.4	0.025	0.60	0.998	0.11	0.52	0.997	5.3 ± 0.1
S24	67.3	0.008	0.57	0.998	0.02	0.55	0.998	5.5 ± 0.4
S25	135.1	0.002	0.24	0.983	− 0.13	0.25	0.991	2.5 ± 1.2
S26	232.9	0.001	0.34	0.994	0.00	0.34	0.994	3.5 ± 0.1
p value	–	–	–	–	–	–	–	< 0.0001
$LSD_{5\%}$	–	–	–	–	–	–	–	1.25

S_0, potentially mineralizable S; k_F, first-order rate constant; S_0k_F, initial potential rate of S mineralization; k_Z, zero-order rate constant

significant correlations between S_0k_F and S mineralization indexes but agrees with results reported for N (Campbell et al. 1991; Burket and Dick 1998) and C mineralization (Riffaldi et al. 1996).

The $S_{min\text{-}10wk}$ correlated with all indexes except with the S_{org}/clay ratio and S-PF, which were not related to any of the evaluated variables. Clay interaction with SOC or S_{org} is described to be the major mechanism protecting S organic pools from microbial breakdown, as sulfate ester (the most labile form of S_{org}) concentration increases with decreasing particle size (Schnug and Haneklaus 1998). However, SOC/clay and S_{org}/clay ratios did not improve the capacity of SOC and S_{org} of predicting $S_{min\text{-}10wk}$ ($r = 0.85$ vs. $r = 0.80$ and $r = 0.68$ vs. $r = 0.19$ for SOC vs. SOC/clay and S_{org} vs. S_{org}/clay, respectively; Table 4). Therefore, the mere division of the organic pools by soil texture (SOC/clay and S_{org}/clay) was inadequate to account for the capacity of soils to protect organic compounds from microbiological mineralization.

The C-PF and S-PF have been proposed as indexes to quantify the size of labile organic C and S pools (Galantini and Rosell 1997; Haynes 2005). Therefore, we expected C-PF and S-PF to be better predictors of S mineralization than SOC and S_{org}, respectively. However, in our study this only occurred for C, as C-PF was slightly better correlated with $S_{min\text{-}10wk}$ than SOC ($r = 0.89$ vs. $r = 0.85$ for C-PF and SOC, respectively; Table 4). This is the first time C-PF is evaluated as an index to predict S mineralization, although it had already been used to predict N mineralization (Domínguez et al. 2016). On the other hand, $S_{min\text{-}10wk}$ was correlated with S_{org} ($r = 0.68$) but not with S-PF (Table 4). Different results were reported by Wyngaard

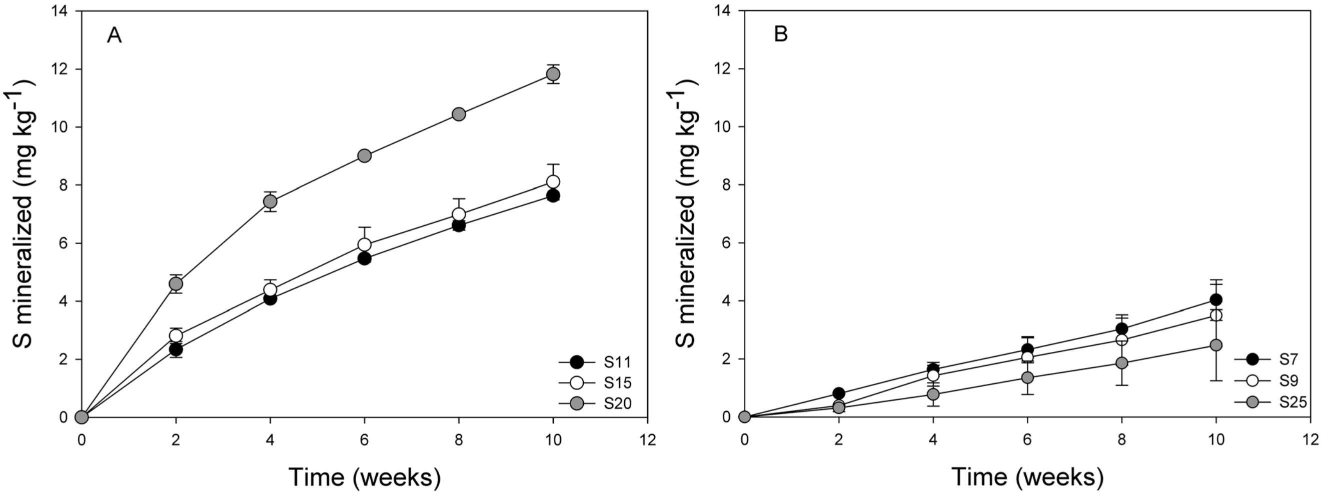

Fig. 1 Examples of different relationships between S mineralized and time of incubation: **a** soils with curvilinear relationship and **b** soils with linear relationship. Vertical bars represent the standard deviation among replications

and Cabrera (2015) who found significant correlations between S_0 and S_{org} ($r = 0.87$) and S-PF ($r = 0.84$). A possible explanation for these contrasting results is that Wyngaard and Cabrera (2015) worked with only four soils, but with very contrasting edaphic properties. Results from other studies suggest that soils with high SOC content generally mineralize large amounts of S (Searle 1992; Riffaldi et al. 2006; Saviozzi et al. 2006), particularly those with low SOC/S_{org} ratio (Kowalenko and Lowe 1975). Along this line, we found a positive correlation between SOC/S_{org} ratio and $S_{min\text{-}10wk}$ ($r = 0.79$; Table 4).

Comparing between incubation indexes, $S_{min\text{-}7d}$ correlated well with $S_{min\text{-}10wk}$ ($r = 0.73$; Table 4), but this correlation was improved when S_{inorg} was not subtracted from the SO_4^{-2}-S concentration determined after incubation ($S_{min\text{-}7d} + S_{inorg}$) ($r = 0.89$; Table 4). The fact that S_{inorg} improved $S_{min\text{-}7d}$ performance as a S mineralization predictor can be explained by the positive relationship between S_{inorg} and $S_{min\text{-}10wk}$ ($r = 0.83$; Table 4), which has been described before by Searle (1992), Reddy et al. (2001), and Niknahad-Gharmakher et al. (2009). The association between $S_{min\text{-}10wk}$ and S_{inorg} can result from the accumulation of mineralized S_{inorg} before soil sampling and/or during the air-drying process (Williams 1967; Tabatabai and Bremner 1972; Ghani et al. 1991). Therefore, when the S_{inorg} released by mineralization is accumulated and not lost from the soil, it can help estimating its S mineralization potential. The use of $S_{min\text{-}7d} + S_{inorg}$ does not only improve the predictive capacity but simplifies the technique as compared with $S_{min\text{-}7d}$.

Finally, N_{an} was highly correlated with $S_{min\text{-}10wk}$ ($r = 0.88$, Table 4), confirming that methods to estimate N mineralization can be used to estimate S mineralization. Moreover, N_{an} cannot only be used to diagnose S availability to crops (Carciochi et al. 2016) but also N availability, as was reported by other authors (Reussi Calvo et al. 2013; Orcellet et al. 2017).

Models to predict S mineralization

Two models for predicting $S_{min\text{-}10wk}$ from soil properties and S mineralization indexes resulted from the stepwise procedure. Both models included SOC, C-PF, and data from an incubation method ($S_{min\text{-}7d} + S_{inorg}$ for model 1 and N_{an} for model 2) (Table 5). The SOC and C-PF account for the total and labile organic pool, respectively, which are the sources for microbiological S mineralization (Scherer 2001), while incubation indexes account for the microbial degradation of the organic pool (Scherer 2001). Between the two proposed models, we suggest the use of model 2, as it uses N_{an} instead of $S_{min\text{-}7d} + S_{inorg}$. This is because the determination of N_{an} is based on an easier technique and it has shown a 10-times lower variability between replicates than $S_{min\text{-}7d} + S_{inorg}$ (Table 2). A third model was proposed as a simplified version of model 2 (Table 5) without considering C-PF, which did not generate a great contribution to the predictive capacity of the model. Thus, the simplified model had a little lower adjusted coefficient of determination than model 2 ($R_a^2 = 0.87$ vs. 0.89, for models 3 and 2, respectively). Similarly, Niknahad-Gharmakher et al. (2009) generated an equation to predict S mineralization that included SOC, but unlike our model, it also accounted for pH, S_{inorg}, and clay content as predictive variables. The inclusion of soil pH is probably a consequence of the alkaline calcareous soils used in the latter study (average pH = 7.8). Even though our model included less variables than the one proposed by Niknahad-Gharmakher et al. (2009), it had a greater predictive capacity ($R_a^2 = 0.87$ vs. 0.84).

Prediction of corn S uptake

Rainfall during corn growing season ranged from 422 to 721 mm depending on site (Table 6). At sites S1, S17, and

Table 4 Pearson correlation coefficients and significance between different *S* mineralization indexes

	S_0	k_F	S_0k_F	k_Z	$S_{min\text{-}10wk}$	$S_{min\text{-}7d}$	$S_{min\text{-}7d} + S_{inorg}$	N_{an}	S_t	S_{inorg}	S_{org}	S_{org}/clay	S-PF	SOC	SOC/clay	SOC/S_{org}	C-PF
S_0	1.00																
k_F	− 0.53	1.00															
S_0k_F	− 0.34	0.93***	1.00														
k_Z	− 0.23	0.77***	0.92***	1.00													
$S_{min\text{-}10wk}$	− 0.25	0.80***	0.93***	1.00***	1.00												
$S_{min\text{-}7d}$	0.05	0.42	0.61	0.75***	0.73**	1.00											
$S_{min\text{-}7d} + S_{inorg}$	− 0.06	0.67*	0.82***	0.90***	0.89***	0.74**	1.00										
N_{an}	− 0.03	0.64*	0.83***	0.89***	0.88***	0.79***	0.88***	1.00									
S_t	− 0.52	0.74**	0.71**	0.67*	0.69**	0.38	0.54	0.47	1.00								
S_{inorg}	− 0.10	0.68**	0.79***	0.82***	0.83***	0.51	0.96***	0.78***	0.52	1.00							
S_{org}	− 0.52	0.73**	0.70**	0.66*	0.68**	0.37	0.52	0.45	1.00***	0.50	1.00						
S_{org}/clay	− 0.54	0.46	0.32	0.16	0.19	0.02	0.01	− 0.04	0.35	0.01	0.36	1.00					
S-PF	− 0.33	0.06	0.01	− 0.18	− 0.16	− 0.13	− 0.19	− 0.17	− 0.09	− 0.19	− 0.09	0.71**	1.00				
SOC	− 0.43	0.79***	0.83***	0.85***	0.85***	0.60	0.75**	0.71**	0.88***	0.70**	0.88***	0.19	− 0.15	1.00			
SOC/clay	− 0.58	0.86***	0.82***	0.78***	0.80***	0.53	0.65*	0.60	0.78***	0.60	0.78***	0.55	0.15	0.89***	1.00		
SOC/S_{org}	− 0.25	0.59	0.68*	0.80***	0.79***	0.67*	0.77***	0.75***	0.59	0.69**	0.58	− 0.07	− 0.25	0.89***	0.77***	1.00	
C-PF	− 0.23	0.81***	0.94***	0.88	0.89***	0.65*	0.84***	0.86***	0.59	0.79***	0.58	0.23	0.07	0.74**	0.72**	0.66*	1.00

***$p < 0.001$; **$p < 0.01$; *$p < 0.05$

Table 5 Models to predict $S_{min\text{-}10wk}$ with different soil variables and *S* mineralization indexes: soil organic carbon (SOC), particulate organic carbon (C-PF); mineralizable *S* determined by short-term aerobic incubation + SO_4^{-2}-S before incubation ($S_{min\text{-}7d} + S_{inorg}$), and mineralizable N determined by short-term anaerobic incubation (N_{an})

Model	Dependent variable	Variable	Parameter value	*p* value	Partial R^2	R_a^2
1	$S_{min\text{-}10wk}$	$S_{min\text{-}7d} + S_{inorg}$	0.425	0.010	0.79	0.90
		SOC	0.076	0.003	0.08	
		C-PF	0.342	0.010	0.03	
		Intercept	0.384			
2	$S_{min\text{-}10wk}$	N_{an}	0.023	0.010	0.77	0.89
		SOC	0.085	0.001	0.10	
		C-PF	0.322	0.020	0.02	
		Intercept	0.990			
3	$S_{min\text{-}10wk}$	N_{an}	0.038	< 0.001	0.77	0.87
		SOC	0.106	< 0.001	0.10	
		Intercept	0.740			

S18, total rainfall was lower than corn water demand (around 550 mm) (Table 6), which may have limited corn growth. The average daily mean temperature was similar to the historical record for each site and did not negatively affect crop growth (data not shown).

Sulfur uptake (S_{uptake}) in aerial biomass by corn is shown for the 18 experimental sites (Table 6). The S_{uptake} ranged from 10.6 to 24.2 kg S ha^{-1}. These values agree with those reported by Pagani et al. (2012) for the same region. The $S_{min\text{-}app}$ varied between 3.2 and 29.4 kg ha^{-1} during the corn growing period, while $S_{min\text{-}app\ (modified)}$ varied from 10.0 to 40.5 kg ha^{-1} (Table 6). These values agree with the S mineralization values reported by Bloem (1998) (10 to 30 kg ha^{-1} year^{-1}) in soils with similar SOC content as those in our study. Additionally, $S_{min\text{-}app\ (modified)}$ represented 1 to 4% of S_{org}, in accordance with the values reported by Freney (1986) and Eriksen et al. (1998).

Linear-plateau relationships between S_{uptake} and S mineralization indexes were observed (Fig. 2). The $S_{min\text{-}10wk}$ had a good

Table 6 Edaphic and climatic properties at 18 cornfield experimental sites including: rainfall during corn growing season (total) and from sowing to V_6 stage, average daily mean temperature during corn growing season, SO_4^{-2}-S content 0–60 cm depth at sowing ($S_{initial}$), and $S_{initial}$ affected by an uptake efficiency ($S_{initial\ (modified)}$), SO_4^{-2}-S content 0–60 cm depth at physiological maturity ($S_{residual}$), *S* uptake in aerial biomass (S_{uptake}), apparent S mineralization ($S_{min\text{-}app}$), and $S_{min\text{-}app}$ accounting $S_{initial\ (modified)}$ ($S_{min\text{-}app\ (modified)}$) (mean ± SD; *n* = 3)

Site	Rainfall (mm)		Temperature (°C)	$S_{initial}$ (0–60) (kg ha^{-1})	$S_{initial\ (modified)}$ (0–60) (kg ha^{-1})	$S_{residual}$ (0–60) (kg ha^{-1})	S_{uptake} (kg ha^{-1})	$S_{min\text{-}app}$ (kg ha^{-1})	$S_{min\text{-}app\ (modified)}$ (kg ha^{-1})
	Total	Sowing to V_6							
S1	422	11	21.9	13.1 ± 0.5	9.0 ± 0.4	9.5 ± 0.2	20.2 ± 2.7	16.6 ± 3.0	20.7 ± 2.9
S2	670	103	18.4	25.6 ± 0.2	11.5 ± 0.1	13.7 ± 3.5	18.5 ± 2.1	6.6 ± 2.4	20.7 ± 2.5
S3	670	103	18.4	18.2 ± 0.6	8.2 ± 0.3	7.7 ± 1.6	19.0 ± 1.4	8.5 ± 3.1	18.6 ± 3.0
S4	702	70	19.8	18.4 ± 0.4	9.8 ± 0.2	11.1 ± 2.2	17.4 ± 1.6	10.2 ± 4.2	18.7 ± 4.1
S5	702	70	19.8	22.0 ± 0.9	11.8 ± 0.5	13.5 ± 3.2	20.1 ± 2.3	11.6 ± 5.6	21.8 ± 5.5
S6	702	70	19.8	18.8 ± 1.2	10.0 ± 0.6	20.3 ± 2.9	20.1 ± 0.6	21.7 ± 2.6	30.4 ± 2.6
S7	721	59	23.4	18.6 ± 1.3	10.4 ± 0.8	5.6 ± 3.1	17.4 ± 3.4	4.4 ± 1.8	12.6 ± 1.3
S8	721	59	23.4	27.1 ± 2.1	15.2 ± 1.2	25.3 ± 1.9	22.3 ± 1.4	20.5 ± 2.5	32.4 ± 2.4
S9	721	59	23.4	22.3 ± 0.8	12.5 ± 0.5	22.5 ± 2.6	15.5 ± 0.6	15.7 ± 1.6	25.4 ± 1.9
S10	721	59	23.4	24.5 ± 1.1	13.7 ± 0.6	24.5 ± 2.0	20.8 ± 1.5	20.9 ± 0.9	31.6 ± 0.5
S11	670	103	18.4	23.2 ± 1.6	10.4 ± 0.7	12.9 ± 0.9	21.4 ± 2.0	11.1 ± 3.8	27.9 ± 3.2
S12	670	103	18.4	20.1 ± 1.2	9.0 ± 0.5	27.6 ± 5.1	21.9 ± 1.6	29.4 ± 4.0	40.5 ± 3.7
S13	670	103	18.4	33.1 ± 2.3	14.8 ± 1.0	19.3 ± 2.7	21.7 ± 1.1	8.0 ± 5.0	26.2 ± 4.2
S14	670	103	18.4	32.5 ± 4.7	14.6 ± 2.1	22.0 ± 4.9	19.2 ± 1.8	8.7 ± 4.0	26.6 ± 3.4
S15	650	5	19.4	12.3 ± 1.8	8.6 ± 1.2	3.8 ± 0.5	15.6 ± 0.6	7.0 ± 1.6	10.7 ± 1.1
S16	650	5	19.4	15.0 ± 1.6	10.5 ± 1.1	7.9 ± 1.5	15.2 ± 2.5	8.1 ± 4.2	12.6 ± 4.0
S17	449	141	19.9	10.5 ± 0.6	3.7 ± 0.2	3.1 ± 0.7	10.6 ± 1.1	3.2 ± 1.2	10.0 ± 1.0
S18	449	141	19.9	19.6 ± 1.0	6.9 ± 0.4	9.7 ± 5.8	24.2 ± 1.2	14.3 ± 7.0	27.1 ± 7.0
p value				< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
$LSD_{5\%}$				2.7	4.9	3.0	1.4	6.0	5.6

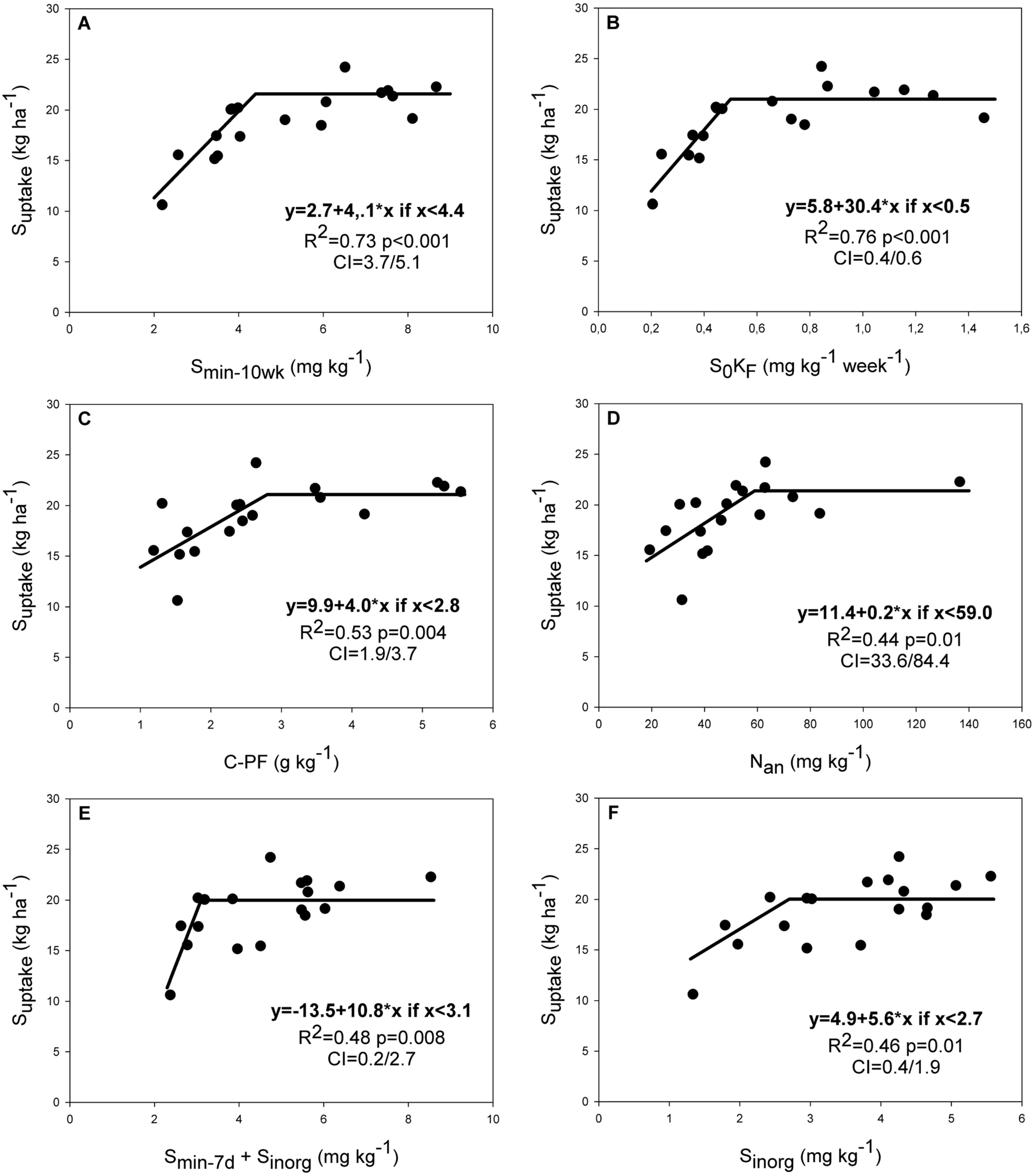

Fig. 2 Linear-plateau models to describe the relationship between S uptake in corn aerial biomass (S_{uptake}) and **a** S mineralized after 10 weeks aerobic incubation ($S_{min\text{-}10wk}$), **b** initial potential rate of S mineralization (S_0k_F), **c** organic C in the particulate fraction (C-PF), **d** N mineralized in anaerobic incubation (N_{an}), **e** the sum of S mineralized after 7 days aerobic incubation and initial SO_4^{-2}-S ($S_{min\text{-}7d} + S_{inorg}$), and **f** initial SO_4^{-2}-S (S_{inorg}). CI is the confidence interval of the critical threshold (0.95). *p* indicates significance of regression

predictive capacity of S_{uptake} ($R^2 = 0.73$, Fig. 2), proving that S mineralization determined by laboratory incubations is related to S mineralization in the field, since this process is the main source of plant available S in unfertilized plots. The S_{uptake} was also associated with S_0k_F ($R^2 = 0.76$; Fig. 2), as with some S mineralization indexes (C-PF, N_{an}, $S_{min\text{-}7d} + S_{inorg}$, and S_{inorg})

(Fig. 2). The threshold values above which maximum S_{uptake} was reached were 2.8 g kg^{-1}, 59 mg kg^{-1}, 3.1 mg kg^{-1}, and 2.7 mg kg^{-1} for C-PF, N_{an}, $S_{min\text{-}7d} + S_{inorg}$ and S_{inorg}, respectively (Fig. 2). Remarkably, previous studies have reported a relationship between S_{uptake} and S_{inorg} for different crops (Scott 1981; Bansal et al. 1983; Eriksen 1997), but none of them related S_{uptake} with S mineralization indexes.

Prediction of $S_{min\text{-}app}$ and $S_{min\text{-}app\ (modified)}$

The stepwise procedure was used to determine a model to predict $S_{min\text{-}app}$ (model 4). Although a significant model was generated, which included C-PF and SOC/clay, it presented a weak predictive capacity ($R^2 = 0.35$). When one variable was considered, C-PF was the only index that was associated with $S_{min\text{-}app}$ (model 5), but with a very low determination coefficient ($R^2 = 0.24$).

Model 4. $S_{min\text{-}app} = 4.43 * \text{C-PF} - 10.58 * \text{SOC/clay} + 11.71$; $R^2 = 0.35$; $p = 0.016$.
Model 5. $S_{min\text{-}app} = 2.45 * \text{C-PF} + 5.64$; $R^2 = 0.24$; $p = 0.038$.

The low predictive capacity of S mineralization indexes for $S_{min\text{-}app}$ is probably a consequence of $S_{min\text{-}app}$ being determined using a simplified balance which does not take into account potential S losses during the crop cycle. Considering that leaching is the main loss process in S cycling (Schoenau and Malhi 2008), in those sites with significant S losses, $S_{min\text{-}app}$ would underestimate S mineralization. To partially solve this problem, $S_{min\text{-}app\ (modified)}$ was calculated using an efficiency for $S_{initial}$ uptake. Thus, the C-PF (model 6) explained 62% of $S_{min\text{-}app\ (modified)}$ variation.

The importance of considering S leaching is observed when comparing models 5 (simplified balance) and 6 (considering $S_{initial}$ uptake efficiency). Moreover, it is likely that $S_{min\text{-}app\ (modified)}$ estimation would be improved by increasing the soil sampling depth below 60 cm, as SO_4^{-2}-S content in subsurface soil is variable between sites and represents an important source of S availability (Haneklaus et al. 2007). Strangely, temperature was not selected as a variable to predict $S_{min\text{-}app}$ or $S_{min\text{-}app\ (modified)}$. This climatic variable is an important factor affecting S mineralization (Eriksen 2009; Schoenau and Malhi 2008) and is usually considered in models to predict N mineralization in the field (Cabrera and Kissel 1988; Egelkraut et al. 2003; Alvarez and Steinbach 2011). However, as the S mineralizable pool size is governed by the temperature of each site (Wang et al. 2006), this variable was indirectly considered. Also, it must be considered that the narrow temperature range between sites in our study (5 °C) (Table 6) may have limited the explicative capacity of temperature over $S_{min\text{-}app}$ or $S_{min\text{-}app\ (modified)}$. Finally, $S_{min\text{-}10wk}$ was also associated with $S_{min\text{-}app\ (modified)}$ (model 7) confirming the relationship between S mineralization in laboratory and in field conditions.

Model 6. $S_{min\text{-}app\ (modified)} = 4.65 * \text{C-PF} + 9.86$; $R^2 = 0.62$; $p < 0.001$.
Model 7. $S_{min\text{-}app\ (modified)} = 3.0 * S_{min\text{-}10wk} + 7.4$; $R^2 = 0.54$; $p < 0.001$.

Finally, it must be considered that S mineralization is a process mediated by microorganisms. Therefore, S mineralization should not only depend on the composition and protection of the mineralizable pool but also on the composition and activity of the microbial community. The importance of these last two microbial variables has been determined in other S cycling processes: recently, Zhao et al. (2017) demonstrated that the abundance and diversity of S-oxidizing bacteria are associated with the oxidation rate of elemental S. In our study, we focused on using edaphic-climatic data to estimate S mineralization ($S_{min\text{-}10wk}$, S_{uptake}, $S_{min\text{-}app}$, and $S_{min\text{-}app\ (modified)}$). However, in future studies, it would be important to analyze the effect of the abundance and diversity of S-mineralizing bacteria on S mineralization under field conditions.

Conclusions

We determined that short and easily measurable indexes as $S_{min\text{-}7d} + S_{inorg}$, C-PF, SOC, and N_{an} can be used to model S mineralization measured by the standard long-term incubation method. Some of these indexes were also associated with S_{uptake} by corn growing under field conditions, suggesting that they can be potentially used as S diagnostic methods. We also evaluated the unprecedented use of a simplified S balance to determine $S_{min\text{-}app}$. However, the S mineralization indexes failed to predict $S_{min\text{-}app}$, probably because this balance does not consider $S_{initial}$ losses. This inconvenience was overcome by developing a new balance accounting for the effect of precipitations over $S_{initial}$ efficiency uptake. Although further studies are necessary to validate the proposed models, they represent a significant advance in predicting S availability to crops under field conditions.

Acknowledgements This work is part of a thesis by Walter D. Carciochi in partial fulfillment for the requirements for a Doctor's degree (Facultad de Ciencias Agrarias, Universidad Nacional de Mar del Plata, Argentina).

Funding information Funding for this research project was provided by Instituto Nacional de Tecnología Agropecuaria-Proyecto Nacional Suelo 1134021, Fondo para la Investigación Científica y Tecnológica PICT 2011-1796, and Universidad Nacional de Mar del Plata AGR447/14.

References

Alvarez R, Steinbach HS (2011) Modeling apparent nitrogen mineralization under field conditions using regressions and artificial neural networks. Agron J 103(4):1159–1168. https://doi.org/10.2134/agronj2010.0254

Bansal KN, Motiramani DP, Pal AR (1983) Studies on sulphur in vertisols. Plant Soil 70(1):133–140. https://doi.org/10.1007/BF02374756

Blair GJ, Chinoim N, Lefroy RDB, Anderson G, Crocker G (1991) A soil sulfur test for pastures and crops. Soil Res 29:619–626

Bloem E (1998) Schwefel-Bilanz von Agraroekosystemen unter besonderer Beruecksichtigung hydrologischer und bodenphysikalischer Standorteigenschaften. FAL Agric Res 192(special):156

Boye K, Nilsson SI, Eriksen J (2009) Net sulfur mineralization potential in Swedish arable soils in relation to long-term treatment history and soil properties. Biol Fertil Soils 45(7):743–751. https://doi.org/10.1007/s00374-009-0390-y

Bremner JM, Keeney DR (1965) Steam distillation method for determination of ammonium, nitrate and nitrite. Anal Chim Acta 32:485–495. https://doi.org/10.1016/S0003-2670(00)88973-4

Burket JZ, Dick RP (1998) Microbial and soil parameters in relation to N mineralization in soils of diverse genesis under differing management systems. Biol Fertil Soils 27(4):430–438. https://doi.org/10.1007/s003740050454

Cabrera ML, Kissel DE (1988) Evaluation of a method to predict nitrogen mineralization from soil organic matter under field conditions. Soil Sci Soc Am J 52(4):1027–1031. https://doi.org/10.2136/sssaj1988.03615995005200040024x

Cambardella C, Elliott E (1992) Particulate soil organic-matter changes across a grassland cultivation sequence. Soil Sci Soc Am J 56(3):777–783. https://doi.org/10.2136/sssaj1992.03615995005600030017x

Campbell CA, LaFond GP, Leyshon AJ, Zentner RP, Janzen HH (1991) Effect of cropping practices on the initial potential rate of N mineralization in a thin black chernozem. Can J Soil Sci 71(1):43–53. https://doi.org/10.4141/cjss91-004

Carciochi WD, Wyngaard N, Divito GA, Reussi Calvo NI, Cabrera ML, Echeverría HE (2016) Diagnosis of sulfur availability for corn based on soil analysis. Biol Fertil Soils 52(7):917–926. https://doi.org/10.1007/s00374-016-1130-8

Domínguez GF, García GV, Studdert GA, Agostini MA, Tourn SN, Domingo MN (2016) Is anaerobic mineralizable nitrogen suitable as a soil quality/health indicator? Span J Soil Sci 6:82–97

Echeverría HE, San Martín NF, Bergonzi R (1996) Sulfur and nitrogen mineralization relationship in agricultural soils (in Spanish, with English abstract). Cienc Suelo 14:107–109

Echeverria HE, San Martin N, Bergonzi R (2000) Rapid methods for assessing potentially mineralizable soil nitrogen (in Spanish, with English abstract.) Cienc Suelo 18:9–16

Egelkraut TM, Kissel DE, Cabrera ML, Adkins W (2003) Predicting N mineralized in a coastal plain field. Nutr Cycl Agroecosyst 66(1):1–12. https://doi.org/10.1023/A:1023306500473

Engels T, Kuhlmann H (1993) Effect of the rate of N fertilizer on apparent net nitrogen mineralization of N during and after cultivation of cereal and sugar beet crops. J Plant Nutr Soil Sci 156:149–154

Eriksen J (1997) Sulphur cycling in Danish agricultural soils: inorganic sulphate dynamics and plant uptake. Soil Biol Biochem 29(9-10):1379–1385. https://doi.org/10.1016/S0038-0717(97)00055-2

Eriksen J (2009) Soil sulfur cycling in temperate agricultural systems. Adv Agron 102:55–89. https://doi.org/10.1016/S0065-2113(09)01002-5

Eriksen J, Mortensen JV, Dissing Nielsen J, Nielsen NE (1995) Sulphur mineralisation in five Danish soils as measured by plant uptake in a pot experiment. Agric Ecosyst Environ 56(1):43–51. https://doi.org/10.1016/0167-8809(95)00632-X

Eriksen J, Murphy MD, Schnug E (1998) The soil sulphur cycle. In: Schnug E (ed) Sulphur in agroecosystems. Kluwer Academic, Dordrecht, The Netherlands, pp 39–74. https://doi.org/10.1007/978-94-011-5100-9_2

Freney JR (1986) Forms and reactions of organic sulfur compounds in soils. In: Tabatabai MA (ed) Sulfur in agriculture. American Society of Agronomy, Madison, WI, pp 207–232

Galantini JA, Rosell RA (1997) Organic fractions, N, P and S changes in an argentine semiarid haplustoll under different crop sequences. Soil Till Res 42(3):221–228. https://doi.org/10.1016/S0167-1987(97)00002-0

Ghani A, Mc Laren RG, Swift RS (1991) Sulphur mineralisation in some New Zealand soils. Biol Fertil Soils 11(1):68–71. https://doi.org/10.1007/BF00335838

Haneklaus S, Bloem E, Schnug E, De Kok LJ, Stulen I (2007) Sulfur. In: Barker AV, Pilbeam DJ (eds) Handbook of plant nutrition. CRC Taylor and Francis, Boca Raton, pp 183–238

Haynes RJ (2005) Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Adv Agron 85:221–268. https://doi.org/10.1016/S0065-2113(04)85005-3

Hollis JM, Hannam J, Bellamy PH (2012) Empirically-derived pedotransfer functions for predicting bulk density in European soils. Eur J Soil Sci 63:96–109

Keeney DR (1982) Nitrogen-availability indices. In: Page AL, Miller RH, Keeney DR (eds) Methods of soil analysis. Part 2. Chemical and microbiological properties. ASA and SSSA, Madison, WI, pp 711–733

Keeney DR, Bremner JM (1962) Nitrogen availability indexes. In: Black CA, Evans DD, White JL, Ensminger LE, Clark FE (eds) Methods of soil analysis, part 2. The American Society of Agronomy, Madison, pp 1324–1341 Unpublished. Agronomy Department, Iowa State University, Ames, Iowa. Cited by Bremner JM 1965

Kowalenko CG, Lowe LE (1975) Mineralisation of sulfur from four soils and its relationship to soil carbon, nitrogen and phosphorus. Can J Soil Sci 55(1):9–14. https://doi.org/10.4141/cjss75-002

Maynard D, Kalra Y, Radford F (1987) Extraction and determination of sulfur in organic horizons of forest soils. Soil Sci Soc Am J 51:801–806

Meisinger JJ (1984) Evaluating plant-available nitrogen in soil-crop systems. In: Hauck RD (ed) Nitrogen in crop production. American Society of Agronomy, Madison, WI, pp 391–416

Meisinger JJ, Calderón FJ, Jenkinson DS (2008) Soil nitrogen budgets. In: Schepers JS, Raun WR (eds) Nitrogen in agricultural systems. ASA-CSSA-SSSA, Agronomy Monograph, vol 49, pp 505–562

Niknahad-Gharmakher H, Machet JM, Beaudoin N, Recous S (2009) Estimation of sulfur mineralization and relationships with nitrogen and carbon in soils. Biol Fertil Soils 45(3):297–304. https://doi.org/10.1007/s00374-008-0332-0

Orcellet J, Reussi Calvo NI, Sainz Rozas HR, Wyngaard N, Echeverría HE (2017) Anaerobically incubated nitrogen improved nitrogen diagnosis in corn. Agron J 109:1–8

Pagani A, Echeverría HE (2011) Performance of sulfur diagnostic methods for corn. Agron J 103(2):413–421. https://doi.org/10.2134/agronj2010.0265

Pagani A, Echeverría HE, Andrade FH, Sainz Rozas HR (2012) Effects of nitrogen and sulfur application on grain yield, nutrient accumulation, and harvest indexes in maize. J Plant Nutr 35(7):1080–1097. https://doi.org/10.1080/01904167.2012.671410

Pirela HJ, Tabatabai MA (1988) Sulphur mineralisation rates and potentials of soils. Biol Fertil Soils 6:26–32

R Core Team (2017) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.r-project.org. Accessed 10 May 2017

Reddy KS, Singh M, Tripathi AK, Swarup A, Dwivedi AK (2001) Changes in organic and inorganic sulfur fractions and S mineralisation in a Typic Haplustert after long-term cropping with different fertiliser and organic manure inputs. Soil Res 39:737–748

Reussi Calvo NI, Sainz Rozas H, Echeverría HE, Berardo A (2013) Contribution of anaerobically incubated nitrogen to the diagnosis of nitrogen status in spring wheat. Agron J 105(2):321–328. https://doi.org/10.2134/agronj2012.0287

Riffaldi R, Saviozzi A, Levi-Minzi R (1996) Carbon mineralization kinetics as influenced by soil properties. Biol Fertil Soils 22:293–298

Riffaldi R, Saviozzi A, Cardelli R, Cipolli S, Levi-Minzi R (2006) Sulphur mineralization kinetics as influenced by soil properties. Biol Fertil Soils 43:209–214

Saviozzi A, Cardelli R, Cipolli S, Levi-Minzi R, Riffaldi R (2006) Sulphur mineralization kinetics of cattle manure and green waste compost in soils. Waste Manag Res 24:545–551

Scherer HW (2001) Sulfur in crop production. Eur J Agro 14(2):81–111. https://doi.org/10.1016/S1161-0301(00)00082-4

Schlichting E, Blume HP, Stahr K (1995) Bodenkundliches Praktikum. Paul Parey, Hamburg, Germany

Schnug E, Haneklaus S (1998) Diagnosis of sulphur nutrition. In: Schnug E (ed) Sulphur in agroecosystems, Part of the series “nutrients in ecosystems”, vol 2. Kluwer Academic, Dordrecht, The Netherlands, pp 1–38. https://doi.org/10.1007/978-94-011-5100-9_1

Schoenau JJ, Malhi SS (2008) Sulfur forms and cycling processes in soil and their relationship to sulfur fertility. In: Jez J (ed) Sulfur: a missing link between soils, crops and nutrition. ASA-CSSA-SSSA, Agronomy Monograph, vol 50, pp 1–10

Scott NM (1981) Evaluation of sulphate status of soils by plant and soil tests. J Sci Food Agric 32(2):193–199. https://doi.org/10.1002/jsfa.2740320216

Searle PL (1992) The extraction of sulphate and mineralisable sulphur from soils with an anion exchange membrane. Comm Soil Sci Plant Anal 23:17–20

Six J, Conant RT, Paul EA, Paustian K (2002) Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. Plant Soil 241(2):155–176. https://doi.org/10.1023/A:1016125726789

Soon YK, Haq A, Arshad MA (2007) Sensitivity of nitrogen mineralization indicators to crop and soil management. Commun Soil Sci Plant Anal 38(15-16):2029–2043. https://doi.org/10.1080/00103620701548688

Tabatabai MA, Al-Khafaji AA (1980) Comparison of nitrogen and sulphur mineralization in soils. Soil Sci Soc Am J 44(5):1000–1006. https://doi.org/10.2136/sssaj1980.03615995004400050026x

Tabatabai MA, Bremner JM (1972) Distribution of total and available sulfur in selected soils and soil profiles. Agron J 64(1):40–44. https://doi.org/10.2134/agronj1972.00021962006400010013x

Tabatabai M, Chae Y (1991) Mineralization of sulfur in soils amended with organic wastes. J Environ Qual 20(3):684–690. https://doi.org/10.2134/jeq1991.00472425002000030030x

Van Biljon JJ, Fouche D, Botha ADP (2004) Threshold values for sulphur in soils of the main maize-producing areas of South Africa. S Afr J Plant Soil 21:152–156

Wang J, Solomon D, Lehmann J, Zhang X, Amelung W (2006) 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

Williams CH (1967) Some factors affecting the mineralization of organic sulphur in soils. Plant Soil 26(2):205–223. https://doi.org/10.1007/BF01880172

Wyngaard N, Cabrera ML (2015) Measuring and estimating sulfur mineralization potential in soils amended with poultry litter or inorganic fertilizer. Biol Fertil Soils 51(5):545–552. https://doi.org/10.1007/s00374-015-1000-9

Zhao F, McGrath S, Crosland A (1994) Comparison of three wet digestion methods for the determination of plant sulphur by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Commun Soil Sci Plant 25(3-4):407–418. https://doi.org/10.1080/00103629409369047

Zhao C, Gupta VVRS, Degryse F, McLaughlin MJ (2017) Abundance and diversity of Sulphur-oxidising bacteria and their role in oxidising elemental sulphur in cropping soils. Biol Fertil Soils 53(2):159–169. https://doi.org/10.1007/s00374-016-1162-0

Zhou W, Li ST, Wang H, He P, Lin B (1999) Mineralization of organic sulfur and its importance as a reservoir of plant-available sulfur in upland soils of north China. Biol Fertil Soils 30:24–250