Note

Characterization of potential CO₂ emissions in agricultural areas using magnetic susceptibility

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Received December 09, 2014 Accepted July 31, 2015 ABSTRACT: Soil CO_2 emissions (fCO $_2$) in agricultural areas have been widely studied in global climate change research, but its characterization and quantification are restricted to small areas. Because spatial and time variability affect emissions, tools need to be developed to predict fCO $_2$ for large areas. This study aimed to investigate soil magnetic susceptibility (MS) and its correlation with fCO $_2$ in an agricultural environment. The experiment was carried out on a Typic Eutrudox located in Guariba-SP, Brazil. Results showed that there was negative spatial correlation between fCO $_2$ and the magnetic susceptibility of Air Dried Soil (MS_{ADS}) up to 34.3 m distant. However, the fCO $_2$ had no significant correlation with MS_{ADS}, magnetic susceptibility of sand (MS_{SAND}) nor clay (MS_{CLAY}). However, MS_{ADS} could be a supplemental mean of identifying regions of high fCO $_2$ potential over large areas. Keywords: magnetism, soil respiration, spatial variability, geostatistics

Introduction

Soil CO₂ emissions (fCO₂) are dependent on soil carbon stock (Scharlemann et al., 2014) which can be easily increased or decreased by the adoption of different agricultural practices (Boeckx et al., 2011). Consequently, spatial and temporal variability for fCO, are high, which complicates efforts to monitor them. The fCO2 is controlled by soil CO, production and transportation to the atmosphere (Fang and Moncrieff, 1999), processes which are affected by factors that determine spatial (physical, chemical, mineralogical and microbiological characteristics of soil) (Saiz et al., 2006; Allaire et al., 2012) and temporal variation in fCO₂. Time variability is mainly influenced by temperature and soil moisture, and their corresponding impact on microbial processes, or their interaction (Yuste et al., 2007). Since soil characteristics that influence fCO2 vary across the landscape, strategies to map and identify locations with different emission potentials are needed. A number of authors have explored emission models for different locations focusing on topographic features (Barrios et al., 2012) and spatial variability of cause and effect relationships for soil properties and fCO, using geostatistics and fractal techniques (Panosso et al., 2012). Both methods need information that is not acquired quickly and accurately across the field.

In this context, magnetic susceptibility (MS) is a rapid technique that can be performed in the field or laboratory which decreases the amount of reagents in mineralogical analysis (Bahia et al., 2014). MS is the degree of magnetization of certain materials (minerals in rocks and soils) in response to a magnetic field application (Dearing, 1994). La Scala et al. (2000) found that the mineralogy of soils influences the potential of fCO₂.

The methods for characterizing locations with different fCO₂ potentials are limited by the time allocated

to evaluation (Teixeira et al., 2013). Larger scale eddy covariance and associated plume methodologies assume that the source strength is constant, a feature that has already been demonstrated to be heterogeneous. In the search for potential covariates, MS is ideal for studies with a large number of samples since it is rapid and inexpensive (Dearing et al., 1996). Our hypothesis was based on a cause and effect relationship between iron oxides and fCO₂ (Bahia et al., 2014). Moreover, MS is directly related to iron oxide mineralogy (Balsam et al., 2004). Thus, because of the different mineralogical composition of soils, MS could be an important property with potential application in the study of the cause and effect relationship between soil mineralogy and fCO₂.

Materials and Methods

The experiment was conducted in Guariba, SP, Brazil (21°21' S; 48°11' W). According to the revised Thornthwaite climate classification system (1948), the local climate is mesothermal humid (B1rB'4a' type) with little water deficiency (mean annual precipitation = 1,432 mm). The experimental area was set up on a Typic Eutrudox (Soil Survey Staff, 1999) with very clayey texture (clay content $> 600 \text{ g kg}^{-1}$). The soil had been cultivated with raw sugarcane under mechanical harvesting for the past 8 years and had generated a large amount of crop residue left on the soil surface (12,000 kg ha⁻¹ yr⁻¹). The experimental area is inserted in a lithostratigraphic division of sandstone-basalt. Geological material in the study area is associated with sandstones of the Bauru Group - Adamantina Formation and basalt of Serra Geral Formation. An irregular 60×60 m grid with 141 sample points was installed within the area with distances of 0.50 to 10.0 m between points (Figure 1). Soil samples were collected at a depth of 0-15 cm.

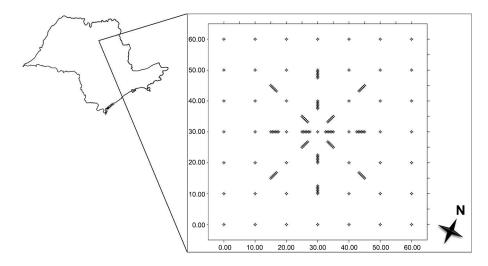


Figure 1 – Sampling scheme used to collect soil samples and evaluate soil CO₂ emissions (fCO₂).

The fCO₂ flux was measured by means of a portable system that monitors changes in CO₂ concentration through infrared radiation analysis inside a chamber placed on the PVC soil collars during the field measurements (Healy et al., 1996). Evaluations were done for 7 days during mornings (8:00 a.m. to 9:30 a.m.), on Julian days 195, 196, 197, 200, 201, 204 and 207 in 2010.

In order to obtain sand and clay fractions for MS evaluation, a treatment with 0.5 N NaOH and mechanical stirring for 10 minutes to disperse the particles was first carried out. Then, the sand fraction was removed through sifting with a 0.05-mm sieve. Silt and clay were separated by centrifugation (1,600 rpm) for a period determined by sample temperatures ranging from 16 to 30 °C. After centrifugation, the suspended clay was flocculated with concentrated HCl, and centrifuged (2,000 rpm for 2 minutes) to yield decanted clay and a supernatant solution with silt. The supernatant solution was discarded and the clay dried in an oven at 105 °C for 24 hours.

MS determinations for ADS (Air Dried Soil) (MS_{ADS}) and sand (MS_{SAND}) and clay (MS_{CLAY}) fractions were made using Bartington MS2 equipment coupled to a Bartington MS2B sensor. The evaluation was done at low frequency (0.47 kHz).

A descriptive statistics was conducted (average \pm standard error; standard deviation; coefficient of variation; minimum; maximum; asymmetry; and kurtosis). Linear and polynomial regressions between MS_{ADS}, MS_{SAND}, MS_{CLAY} and fCO₂ were analyzed. Spatial variability was evaluated by GS+ 9.0 software. Experimental semivariogram modeling was based on the theory of regionalized variables, estimated by the following equation:

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[Z(x_i) - Z(x_i + h) \right]^2$$
(1)

where: $\hat{\gamma}$ (h) is the experimental semi variance for an h distance; z (x_i) is the property value at the I point; and N (h) is the number of pairs of points separated by an h distance. The semi-variogram represents variable spatial continuity as a function of the distance between two locations. Spatial dependency between fCO₂ and magnetic susceptibilities of MS_{ADS}, MS_{SAND}, and MS_{CLAY} were modeled by means of cross-semivariograms, and estimated by means of the following equation:

$$\hat{\gamma}_{Zy}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[Z(x_i) - Z(x_i + h) \right] \left[y(x_i) - y(x_i + h) \right]$$
(2)

where: $\hat{\gamma}_{z_y}(h)$ is the experimental cross semi variance for an h distance; z (x_i) the value of the main variable (the one to be estimated) at point I; y (x_i) the value of the secondary variable at i point; and N (h) the number of pairs of points separated by an h distance. Note that a simple variogram is a particular case of a cross variogram wherein the semi-variance is calculated for one property only. Consequently, it is considered a measurement tool of variable spatial autocorrelation. In this study, we used adjusted spherical and Gaussian models; the best-fitted model to the variogram was set up in a lower Residual Sum of Squares (RSS), and a Coefficient of determination (R^2) obtained for model adjustment.

Results and Discussion

The fCO $_2$ had an average of 1.69 \pm 0.08 μ mol m $^{-2}$ s $^{-1}$, with a minimum value of 0.34 μ mol m $^{-2}$ s $^{-1}$ and a maximum of 4.49 μ mol m $^{-2}$ s $^{-1}$ (Table 1) which is lower than that of Panosso et al. (2012) who studied sugarcane cultivation in red Oxisols. The lack of rainfall prior to the experimental period, the low soil organic matter content (4.75 \pm 0.05 g dm $^{-3}$), and the high soil compaction represented by a bulk density average of 1.50 \pm 0.01

Table 1 – Descriptive statistics for fCO_2 , MS_{ADS} , MS_{SAND} and MS_{CLAY} .											
	Mean	ASE	SD	CV	Min.	Max.	Asymmetry	Kurtosis			
fCO ₂	1.69	0.08	0.97	57	0.34	4.49	1.03	0.33			
MS_{ADS}	2064	9.43	112	5	1844	2522	0.80	2.00			
${\sf MS}_{\sf SAND}$	2426	29.64	352	15	1703	4202	0.99	3.91			
MS _{CLAY}	1452	7.92	94	6	1029	1729	0.68	2.67			

 $fCO_2 = soil\ CO_2$ emissions (µmol $m^{-2}s^{-1}$); MS = Magnetic Susceptibility ($10^{-8} \times m^3$ kg⁻¹); ADS = Air Dried Soil; ASE = standard error of mean; SD = Standard Deviation; CV = coefficient of variation (%); Min = minimum value; Max = maximum value

g cm $^{-3}$ as was noted by Teixeira et al. (2013), could be an explanation for the low average emission. The fCO $_2$ coefficient of variation (CV) was 57 %, which is typical for this property (La Scala et al., 2000). Brito et al. (2009), who obtained similar results in sugarcane areas, observed a mean CV of 55 % for fCO $_2$.

For MS_{ADS}, an average of 2,064 \pm 9 × 10⁻⁸ m³ kg⁻¹ was obtained, with a minimum value of $1,844 \times 10^{-8}$ $m^{\scriptscriptstyle 3}$ $kg^{\scriptscriptstyle -1}$ and a maximum of 2,522 \times $10^{\scriptscriptstyle -8}$ $m^{\scriptscriptstyle 3}$ $kg^{\scriptscriptstyle -1}.$ The MS_{SAND} had an average of 2,426 \pm 352 \times 10⁻⁸ m³ kg⁻¹, with a minimum value of 1,703 \times $10^{-8}\ m^3\ kg^{-1}$ and a maximum of 4,202 \times 10⁻⁸ m³ kg⁻¹. Whereas for MS_{CLAY}, the average was of $1,452 \pm 94 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ with a minimum of $1,029 \times 10^{-8}$ m³ kg⁻¹ and a maximum of $1,729 \times 10^{-8} \,\mathrm{m^3\,kg^{-1}}$. The highest average value of MS- $_{\mathrm{SAND}}$ is attributable to the primary mineral, magnetite, in the soil fine sand fraction, which have magnetic behavior more evident compared to the second mineral maghemite, found in the clay fraction (Fabris et al., 1998) and produced by oxidation with its formation intensified by fire (Ketterings et al., 2000; Terefe et al., 2008). Thus, the variations of MS values can be explained by minerals in soils derived from basalt and the historical management of sugar cane burning in the harvesting system.

The ${
m MS}_{
m ADS}$ was lower than ${
m MS}_{
m SAND'}$, since the first resulted from the interaction of various magnetic fields with different intensities, some even with negative intensity. While for ${
m MS}_{
m SAND'}$ only the MS of these minerals in this fraction is accounted for, and there was no interaction with other magnetism types, which resulted in the highest value. Matias et al. (2014) observed similar results in Oxisols and found ${
m MS}_{
m ADS}$ average values between 2,300 \times 10⁻⁸ m³ kg⁻¹ and 2,700 \times 10⁻⁸ m³ kg⁻¹.

We noted that the CVs of $MS_{ADS'}$ $MS_{SAND'}$ and MS_{CLAY} are much lower when compared to fCO_2 , which can be explained by a greater uniformity of MS within the area studied. Barrios et al. (2012), studying the potential of MS in identifying of landscape compartments on a detailed scale in Jaboticabal-SP, reported similar CVs for $MS_{ADS'}$ MS_{SAND} and MS_{CLAY} that were, respectively, from 5 to 13 %, 11 to 18 %, and 5 to 12 %, depending on the landscape segment. -

No models of linear and polynomial regression (p > 0.05) were found between fCO $_2$ and MS $_{\rm ADS}$, MS $_{\rm SAND}$ and MS $_{\rm CLAY}$. This fact may be related to the high coefficients of variation found for fCO $_2$ (La Scala et al., 2000; Ray-

ment and Jarvis, 2000; Adachi et al., 2009), which make it difficult to establish linear and polynomial relations. Consequently, the use of geostatistics is of great importance, when recording spatial correlations between soil attributes, in the production of the most accurate mappings for fCO₂. Bahia et al. (2014) illustrated the spatial dependence between mineralogy and fCO₂.

The simple semivariogram models that best fit were the spherical (fCO_2, MS_{SAND}) and MS_{CLAY} and the Gaussian (MS_{ADS}) as revealed by low values for RSS and high values for R² (Table 2). Kosugi et al. (2007) and Santos et al. (2013) adjusted similar semivariogram models for fCO_2 and MS_{ADS} . In addition, the spherical model is associated with abrupt changes in the pattern of variability (Teixeira et al., 2012), especially in relation to more distal points. On the contrary, the Gaussian model is related to small changes in the pattern of variability (Teixeira et al., 2012).

Range values were for fCO $_2$ (37.3 m), MS $_{ADS}$ (37.7 m), MS $_{SAND}$ (5.3 m) and MS $_{CLAY}$ (5.6 m) (Table 2). Similar range values were also found by Brito et al. (2010) in a soil derived from similar geologic parent material. The fCO $_2$ and MS $_{ADS}$ showed very tight range values, suggesting a potentially similar pattern of variability, which was not observed for MS $_{CLAY}$ and MS $_{SAND}$, that attained range values quite different from fCO $_2$. According to the classification proposed by Cambardella et al. (1994), when the ratio is lower than or equal to 25 %, spatial dependence is considered strong; between 25 and 75 %, moderate; and higher than 75 %, weak. In this study, we found a strong degree of spatial dependence for MS $_{ADS}$ and moderate for fCO $_2$, MS $_{SAND}$ and MS $_{CLAY}$.

Furthermore, negative spatial dependence was found between fCO_2 and MS_{ADS} for a distance of 34.3 m (Figure 2A). The Gaussian model was the best fit to the $fCO_2 \times MS_{ADS}$ cross semivariogram, while other values of MS_{SAND} and MS_{CLAY} were not correlated with fCO_2 , which is indicated by the absence of spatial dependence (pure nugget effect). However, even this study had shown spatial correlation between MS_{ADS} and fCO_2 , isotropic models were found for all properties studied, which can be verified in studies conducted by Teixeira et al. (2013) and Bicalho et al. (2014). However, these results differ from studies conducted by Bahia et al. (2014).

The fCO₂ and MS_{ADS} spatial dependence could be associated with soil porosity and bulk density, which are dependent on sand and clay contents. Higher values for total porosity and lower bulk density promote enhanced capacity for gas to diffuse throughout the soil and, consequently, increase fCO₂. The literature has shown that MS_{ADS} is an excellent pedological indicator of clay content in tropical soils for areas with iron content of soil between 4 and 18 % (Siqueira et al., 2010, 2014; Matias et al., 2014). Clay content is related to microporosity (Aringhieri, 2004) and consequently to total porosity. According to Cambardella et al. (1994), the higher spatial dependence in soil attributes is correlated with interactions between parental material, climate and to-

Table 2 – Models of semivariogram and parameters.

Variables	Model	0	$C_0 + C_1$	Range (m)	$C_0/(C_0+C_1)*100$	Model		Cross-validation	
	Model	C_0				R ²	RSS	а	b
fCO ₂	Spherical	0.14	0.37	37.30	38	0.89	0.006	0.69	0.80
MS_{ADS}	Gaussian	0.09	0.38	37.76	24	0.95	0.008	0.00	1.02
MS _{SAND}	Spherical	1.90	3.76	5.27	51	0.81	0.440	0.06	0.78
MS _{CLAY}	Spherical	0.47	0.70	5.61	67	0.70	0.020	-0.61	1.05

 C_0 = nugget effect; C_0+C_1 = Sill; $C_0/(C_0+C_1)$ = Degree of Spatial Dependence; R^2 = coefficient of determination; RSS = Residual Sum of Squares; a = intercept coefficient; b = slope coefficient.

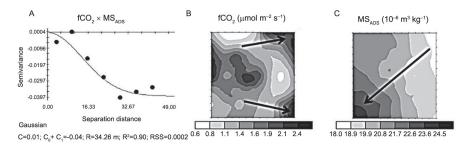


Figure 2 – Cross semivariogram of soil CO_2 emissions (f CO_2) versus magnetic susceptibility of air dried soil (MS_{ADS}) (A) and variability maps of f CO_2 (B) and MS_{ADS} (C) at a depth of 0.0-0.2 m.

pography. However, moderate spatial dependence is correlated with extrinsic factors like agricultural field management.

Thus, compartments with higher MS_{SAND} and MS_{CLAY} will show greater pore spaces, which might favor an easier gas exit, resulting in higher fCO₂ rates. Teixeira et al. (2013), who studied spatial estimates of fCO₂ through soil density, found lower range values (18.95 to 21.37 m) and degrees of spatial dependence (0.07 to 0.17) for cross semivariograms of fCO₂ × soil density. This suggests that MS_{ADS} may have greater potential for the production of spatial estimates of fCO₂ relative to soil bulk density, as well as being a technique which is faster, easy to handle and low-cost for the examination of larger field areas.

Spatial distribution maps (Figure 2B and C) confirm the result of the cross semivariogram, showing that there is a trend of increasing fCO_2 (direction of the arrow), whereas MS_{ADS} increases in the reverse direction.

The results of the interaction of spatial variability between MS_{ADS} and fCO₂ indicated that MS_{ADS} can be an interesting alternative for research programs that study the cause and effect relationship between mineralogy and fCO₂, such as Panosso et al. (2011). Additionally, studies on the characterization of the spatial variability of fCO₂ can also be drawn from these results in order to help establish the proportion in samples of MS_{ADS} to fCO₂, as developed for MS_{ADS} and clay content by Siqueira et al. (2014). This information may assist further studies and clarify the relationship between landscape use and global climate changes by providing information to support decisions about mitigation and adaptation strategies (Bayer et al., 2006; De Figueiredo and La Scala, 2011).

Conclusions

Air Dried Soil Magnetic Suceptibility (MS_{ADS}) had spatial dependence on fCO₂ up to a distance of 34 meters indicating that this information may be used to define fCO₂ spatial variability, especially for research projects that study the cause and effect of the relationship between mineralogy and fCO₂.

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