Research Article

Organic matter of tropical soil with coffee growth in CO$_2$ enriched atmosphere

Abstract

The increase of atmospheric CO$_2$ should result in higher carbon fixation by plants of the C3 photosynthetic cycle, such as coffee. However, not much is known about the relationship between atmospheric CO$_2$ increase, higher carbon fixation through photosynthesis and the potential carbon sequestration in soil. Based on the hypothesis that there will be greater stabilization of carbon in soil due to increase of atmospheric CO$_2$ concentration, the study was carried a field coffee grown area with FACE (Free-Air Carbon dioxide Enrichment) system. The CO$_2$ enrichment treatment maintained the concentration of this gas 200 μmol mol^{-1} above the ambient value. The stocks of carbon and nitrogen in soil and some attributes related to the humification of organic matter were evaluated 43 months after the beginning of the experiment. In addition, the decomposition of residues of coffee plants (leaves) and the emission of N$_2$O were also evaluated. The stocks of carbon and nitrogen in soil of at 0-5 cm layer were in average 18% higher (2.6 Mg ha^{-1} carbon and 0.2 Mg ha^{-1} nitrogen) in CO$_2$ enrichment treatment. As the decomposition of vegetal remains was not affected by atmospheric CO$_2$ enrichment, the increase of carbon and nitrogen in soil was due to the greater contribution of vegetal material, which resulted in a less humic organic matter. In the equilibrium between carbon soil stabilization and N$_2$O emission, the enrichment of atmospheric CO$_2$ in the coffee crop resulted in negative feedback for global warming due to the increased sequestration potential of carbon by soil.

Keywords: *Coffea arabica*, carbon stock, humic substances, free-air carbon dioxide enrichment, humification index

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Introduction

The atmospheric concentration of CO$_2$ before Industrial Revolution was stable and with an approximated value of 270 μmol mol^{-1},[1,2] however with the increase of emissions of this gas to the atmosphere due to coal burning and other fossil fuels, atmospheric concentration of CO$_2$ began to rise, currently reaching concentrations around 400 μmol mol^{-1} [2–4] and studies indicate a forecast for the year 2100 of 700 μmol mol^{-1}.[4]

This increase in [CO$_2$] may influence many aspects of human and natural world, but its effects on agricultural production may be particularly important.[4] This scenario of elevation of CO$_2$ concentration leads agronomic research to investigate the effects of this increase on agricultural crops, since CO$_2$ constitutes a primary substrate for photosynthesis[5] and its elevation might stimulate plant biomass production, and consequently increase soil carbon (C) concentration, which contributes to the increase of soil organic matter.[6]

With the increase of studies and hypothesis about agriculture impacts caused by atmospheric CO$_2$ concentration increase, technology development was researched that could suppress the necessity of testing these hypothesis in free-air field, leading to the development of FACE technology (Free-Air Carbon Dioxide Enrichment).[7–9]

Over time, with FACE experiment studies, it is already possible to observe some important results such as increased carbon uptake by plants,[10,1] impacts on photosynthetic nitrogen (N) efficiency use,[8,11–13]

the increase in agricultural production due to a possible effect of CO$_2$ fertilization was lower than expected,[1,14,15] the stimulation of carbon uptake by elevation of [CO$_2$] in C4 plants is indirect and occurs only in water-restriction conditions,[1] C3 and CAM plants show a positive response to the increase of CO$_2$ concentration during growth, whereas C4 plants have a negative response.[16,17]

However, the dynamics of organic matter and nutrients in cultivated soil under high CO$_2$ concentration is still poorly studied and understood, especially in tropical climate regions where organic matter dynamic is high.[17] Studies have shown that with a higher carbon supply the plants tend to increase the efficiency of macronutrients use, such as nitrogen, due to the greater activity of the enzyme Rubisco.[18]

Therefore, understanding the impact of increasing atmospheric CO$_2$ on crop, soil and SOM dynamics is necessary to formulate a possible adequate strategy for food safety and address environmental concerns.[17]

Coffee is one of main agricultural commodities in Brazil, the largest world producer,[19] four countries in 2013 were responsible for 64.8% of world production: Brazil (33.2%), Vietnam (16.4%), Indonesia (7.8%) and Colombia (7.3%), all in tropical regions.[20] According to some authors, climate change may directly interfere in coffee production.[9,20,21] The objective of this study was to investigate the possible effects of CO$_2$ increase in the atmosphere through FACE experiment in content and quality of soil organic matter with coffee cultivation.

Material and methods

The field experiment was conducted at Embrapa Environment Experimental Field, located in Jaguariúna, São Paulo State, Brazil (latitude 22°43'06" S, longitude 47°01'09" W and altitude 570 m). The climate is humid subtropical, a Cfa type according to the Köppen classification, with hot rainy summers and cold dry winters. The soil at the experimental area was Dark Red Dystroferric Oxisol (loamy/clayey-textured).

It used a coffee cultivar Catuaí IAC-144 (*Coffea arabica* cv. Catuaí Vermelho IAC-144). Coffee seedlings were transplanted in March 2010 with spacing of 3.5 m between rows and 0.6 m between plants with annual fertilization in the crown projection[9] and brachiaria (*Brachiaria decumbens*) without fertilization,[21] no irrigation was used for this experiment. The applications of limestone and fertilizers were based on the recommendation used for the State of São Paulo[22] for expected yield of 30 sacks per hectare.[21]

The experimental used was a randomized block design, in which twelve ring plots spaced 70 m apart from one another and with a diameter of 10 meters were constructed. Six out of twelve ring plots received application of carbon dioxide (FACE) and the other six remained as controls (Ambient), which means, without application of CO₂.

The atmospheric enrichment with CO₂ was initiated in August 2011. The application of CO₂ was performed from a vertical tank with copper pipes leading the gas to the ring plots (Figure 1). The gas release was controlled so that the atmosphere had a concentration of approximately 200 μmol mol⁻¹ CO₂ higher than the natural atmosphere concentration. The speed and direction of the wind were constantly monitored to determine the gas injection flow, with the purpose of applying it only inside each ring, thus obtaining the values of 550 μmol mol⁻¹ of CO₂ for the treatment (FACE) and 390 μmol mol⁻¹ of CO₂ for the control treatment (Ambient), which corresponds to the value measured by the sensor in the normal situation of the site. Further details of the experiment can be found in Ghini et al.[9]

Soil sampling was carried out in March 2015, that is, 43 months after the beginning of CO₂ application. Undisturbed soil samples were collected for density analysis and deformed soil samples to determine the total C, C concentration associated in humic fractions of soil organic matter and humification index of soil organic matter.

Within each ring plot a trench was opened to remove undisturbed soil samples up to 1 m deep using metal kopeck cylinders with an internal capacity of 99.64 cm³. In the 0-5, 5-10, 10-20, 20-40 cm layers, the trenches were located perpendicular to the coffee line to allow sampling of the soil in the following positions: next to the crop line, in the center of the line and in intermediate positions between the crop lines and the center of the interline. For the other layers, 40-60, 60-80 and 80-100 cm, undisturbed soil samples were collected in only one portion of each treatment, open in the area outside the CO₂ application ring. This decision was based on the fact that changes in soil density at these depths are not expected during this experiment period.

Soil density was determined gravimetrically by the ratio between the mass of the oven dried sample at 105-110 ° C and the kopeck ring volume.[23] The deformed soil samples were collected using auger, in the same layers and positions collected for density. Nine points per ring plot were sampled, three in each of the previously mentioned positions, in order to compose the representative sample of the ring plot. After collection, the soil samples were air dried, homogenized and passed in a sieve with a 2 mm mesh. Then, the soil samples were grounded and passed through a 0.150 mm mesh (100-mesh) for quantification of total C and N concentration, determined by the dry combustion method, by CN elemental analyzer (TruSpec CN LECO®), from these values obtained the C:N ratio.

On the basis of these results and the results obtained from soil density, the stocks of C and N for each depth was calculated according to the equation:

C or N stock = 1000000×C×(SD) ×·L

Where:

C or N stock = kg ha⁻¹

C=concentration of C or N in soil (%)

SD=soil density (g cm⁻³)

L=layer thickness (cm)

Possible changes in soil organic matter quality were investigated through chemical fractionation and humification index. The chemical fractionation of the soil organic matter separated it in fulvic acids (FA), humic acids (HA) and humin fraction (HU), performed in samples of layers 0-5, 5-10, 10-20, 20-40 and 40-60 cm as a function of the differential solubility in acidic and alkaline media[24] and the determination of carbon via oxidation.[25]

The method used for quantification of humification index was laser-induced fluorescence (LIF) spectroscopy in intact soil sample[26] and it was used in samples of soil analyzed for total of C (0-5, 5-10, 10-20, 20-40 and 40-60 cm). These samples were pressed into pellets of 1 cm diameter and 2 mm thickness and 0.5 grams of weight. The equipment has been configured for the minimum wavelength 435 nm and maximum 800 nm. The exposure time was 100 ms and luminous intensity minimum was 0 and maximum was 500 nm. The humification index of soil organic matter was then obtained by calculating the area under the emission curve divided by the total soil carbon concentration.

In order to observe if there was influence of atmospheric enrichment of CO₂ on the decomposition of the coffee leaves in soil overturned by the harvest, in July 2014, 10 litterbags per ring plot in the dimensions of 20 x 20 cm were installed in the coffee growing line, with mesh screen of 35, according to Bocock and Gilbert,[27] filled with the coffee leaves accumulated on the ground in the 2014 harvest, dried and homogenized, with initial dry mass of 20 g, equivalent to 5000 kg ha⁻¹.[28]

The litterbags were collected at 0, 14, 36, 60, 90, 119, 179, 291 and 362 days after field installation. At each collection, the samples were randomly taken from the field, cleaned, dried and weighed. Remaining dry biomass (kg ha⁻¹), nitrogen and carbon concentration were determined by the dry combustion method, using CN elemental analyzer (TruSpec CN LECO®).

The cumulative emissions of N₂O and CO₂ were measured using the closed-chamber method[29,30] for two consecutive seasons (2013/2014 e 2014/2015). Gas chambers installed in the experimental ring plots were made of PVC cylinders (30 cm diameters), to collect the gas sample from the third fertilizer application in middle February until

harvesting, around June. Each ring plot had three chambers locate in the canopy projection to evaluate either the N$_2$O emission from the fertilizer and the CO$_2$ from the soil respiration, two with and one without fertilizer application, for the enrichment of CO$_2$ and ambient CO$_2$ concentration treatment. The first sampling events occurred immediately after fertilizer application and every two or three days thereafter until harvesting.

Changes in the headspace gas concentrations were measured at a time interval of 0-15-30 min after the camber closure. N$_2$O and CO$_2$ concentration was analyzed by gas chromatography (Thermo Scientific™ TRACE™ GC systems). Flux rates of N$_2$O and CO$_2$ were calculated using the slope of the temporal changes in gas concentration within the closed chamber, considering chamber volume and surface area of the chamber. Daily results from each chamber were expressed in emission per chamber, and then extrapolated to emission per hectare. Cumulative emission was calculated by linear interpolation between subsequent daily fluxes.

Statistical analysis of the results was done using variance analysis (ANOVA), considering the randomized block design, and as a factor of interest variation the application or not of CO$_2$. In case of significant effect of the interest factor, the Student's t-test was applied at a significance level of 5% ($p < 0.05$) to compare the means.

Results and discussion

Soil carbon and nitrogen stock

After 43 months of experimentation, there was an increase in soil C and N concentration only in the most superficial layer (0-5 cm) as a function of CO$_2$ enrichment (Table 1). In 0-5 cm layer, the C and N concentrations in the treatment with atmospheric CO$_2$ enrichment (FACE) were 18% higher for both, in comparison with those observed in control treatment.

In general, concentration of C and N decreased along the soil profile, which is expected to happen with organic matter gradient as a function of soil depth. The C:N ratio of soil was not changed with treatments and the variation in soil profile (C:N from 12.0 to 13.7) could be considered low (Table 1).

The plant dry matter, whether from shoot or root, has an important role in carbon input in soil, so the increase in photosynthetic rate and, consequently, the increase of the dry matter production, can result in a higher contribution of carbon in soil.[31] Ghini et al.[9] in a study conducted in the same area two years after the beginning of the experiment, observed an increase in photosynthesis and coffee productivity due to the atmospheric enrichment of CO$_2$, which may be the cause of the increase of the C concentration in the observed superficial layer in this present study.

Other authors also observed increases in soil C concentration due to CO$_2$ enrichment. Dijkstra and Morgan (2012) presented a compilation of 27 studies with atmospheric enrichment of CO$_2$ and observed the occurrence of increases in C concentration in soil surface layer, some studies up to the 20 cm layer, in 74% of these studies.

The soil density was not influenced by atmospheric CO$_2$ enrichment (Table 2). The values of density up to 40 cm depth are within the appropriate range (1.25 to 1.40 gcm^{-3}) for good root development without the occurrence of physical impediments.[32] The soil density in the superficial layers can decrease when there is a constant supply of vegetal residues, since these residues present low density and greater porosity when compared to the mineral fraction of the soil.[33]

Due to the changes in C and N concentration in the soil and the absence of soil density response to CO$_2$ treatments, the results of C and N stocks followed the results for the levels (Table 2). The modeling study about the dynamics of C in soil by Graff et al.[34] with a compilation of 59 works using FACE-type experiments in the field, reached the result that the atmospheric enrichment of CO$_2$ promotes a 1.2% increase of C in the layer up to 20 cm. However, the authors note that there is few long-term data with a FACE-type experiment. Smith[35] using the "Rothamsted Carbon Model" soil organic carbon model estimated that it would take seven to ten years for C changes to occur due to the enrichment of CO$_2$ in the atmosphere to a depth of 20 cm.

Table 1 Total carbon and nitrogen concentration and C:N ratio in soil as a function of CO$_2$ level in atmosphere in coffee growing area

Layer (cm)	Soil Carbon g kg^{-1}		Soil Nitrogen g kg^{-1}		C:N Ration --	
	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]
0-5	34.87 a	29.62 b	2.62 a	2.22 b	13.37 a	13.48 a
5-10	21.97 a	20.33 a	1.62 a	1.52 a	13.53 a	13.54 a
10-20	21.48 a	25.16 a	1.62 a	1.78 a	13.20 a	13.70 a
20-40	15.13 a	15.14 a	1.22 a	1.22 a	12.51 a	12.38 a
40-60	14.84 a	13.45 a	1.17 a	1.08 a	12.84 a	12.44 a
60-80	13.22 a	11.26 a	1.02 a	0.93 a	13.00 a	11.99 a
80-100	12.77 a	12.18 a	0.98 a	0.97 a	12.61 a	12.91 a

Averages followed by different letters in same line are statistically different by Student's t-test ($p < 0.05$)
[1]Treatment with atmospheric CO$_2$ enrichment, concentration of 550 µmol mol^{-1} of CO$_2$
[2]Treatment with ambient air, concentration of 390 µmol mol^{-1} of CO$_2$

Table 2 Soil density and soil carbon and nitrogen stock as a function of CO_2 level in atmosphere in coffee growing area

Layers (cm)	Soil density g cm^{-3}		Soil carbon stock Mg ha^{-1}		Soil nitrogen stock Mg ha^{-1}	
	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]
0-5	1.27 a	1.32 a	22.12 a	19.57 b	1.65 a	1.45 b
5-10	1.42 a	1.39 a	15.59 a	14.09 a	1.15 a	1.04 a
10-20	1.43 a	1.43 a	30.63 a	36.23 a	2.32 a	2.56 a
20-40	1.41 a	1.41 a	42.46 a	42.68 a	3.40 a	3.45 a
40-60	1.33*	1.31*	39.29 a	35.63 a	3.06 a	2.86 a
60-80	1.28*	1.29*	34.04 a	28.97 a	2.61 a	2.41 a
80-100	1.26*	1.29*	32.62 a	31.12 a	2.52 a	2.47 a

Averages followed by different letters in same line are statistically different by Student's t-test ($p < 0.05$)

[1]Treatment with atmospheric CO_2 enrichment, concentration of 550 μmol mol-1 of CO_2

[2]Treatment with ambient air, concentration of 390 μmol mol-1 of CO_2

Chemical fractionation of SOM and humification index

It was observed an increase of the C concentration associated with fractions FA and HA in the layer 0-5 cm with atmospheric CO_2 enrichment and no differences were noticed in the HU fraction (Figure 1). This result indicates that there was an increase in the most labile forms of soil C, since organic compounds presented in FA and HA fractions are more likely to mineralize C when compared to compounds of the HU fraction.[36] It was also observed an increase in C concentration associated with the HA fraction in the 10-20 cm layer with atmospheric CO_2 enrichment.
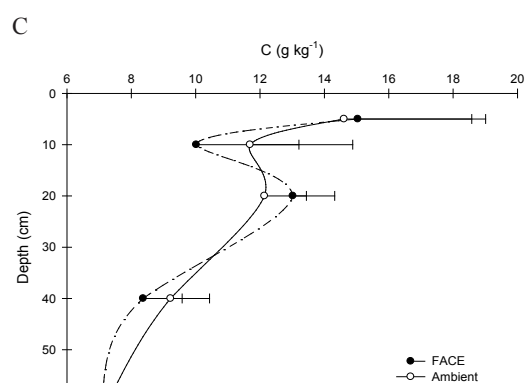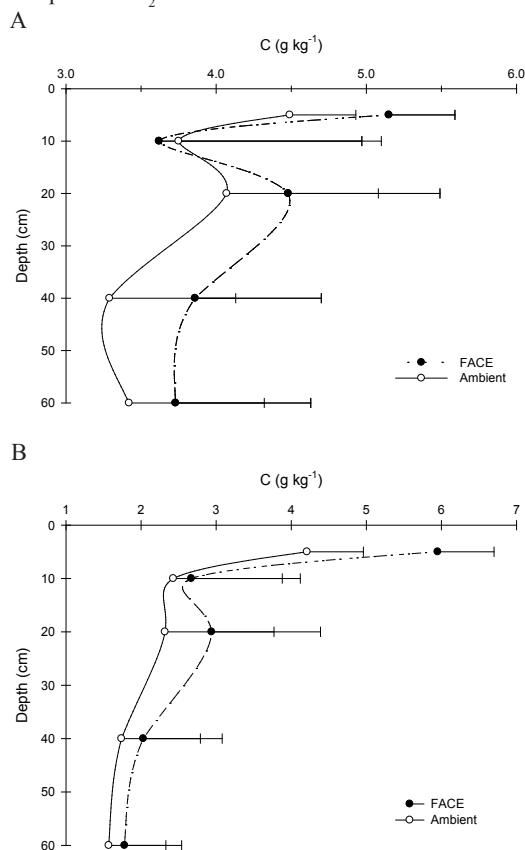
A

B

C

Figure 1 Carbon concentration associated to fulvic acid fraction (A), humic acid fraction (B) and humin fraction (C) as a function of CO_2 level in atmosphere in coffee growing area. Error bars = LSD (Least Significant Difference) of Student's t-test ($p < 0.05$).

The increase, in surface layer, of C concentration in the most labile fractions of organic matter with atmospheric CO_2 enrichment is due to the increase of fresh organic material[9] and also the reduction of the mineralization rate of soil organic matter in the field.[37] The reduction of the mineralization rate of soil organic matter can be indirectly influenced by atmospheric CO_2 enrichment due to the increase of the photosynthesis rate of the plant[9] and, consequently, a higher requirement for water, causing a reduction in soil moisture. With the reduction of moisture, there is a slower mineralization of soil organic matter. A study at controlled temperature and moisture soil conditions showed no changes at the rate of soil organic matter mineralization due to atmospheric CO_2 enrichment.[37]

In a study about the evaluation of soil fertility in the same area, Maluf et al.[21] observed that the pH of soil in the 0-5 cm layer of the treatment with atmospheric CO_2 enrichment was higher when compared to the control. The authors suggested that this increase in pH can be caused by complexation of Al^{3+} ion by organic compounds, this fact that can be proven by the increase of the fractions FA and HA in the treatment with atmospheric CO_2 enrichment, because these fractions present high power of complexation with ions.[38]

The results of the increase of less humi organic compounds in the superficial layer due to the atmospheric CO_2 enrichment is in

agreement with the one observed in the analysis of the humification index of soil organic matter. In the treatment with CO$_2$ application the humification index presented 18.21% lower than the treatment with ambient air (Figure 2), for the first layer. In the other layers, there was no difference between the means of the treatments.
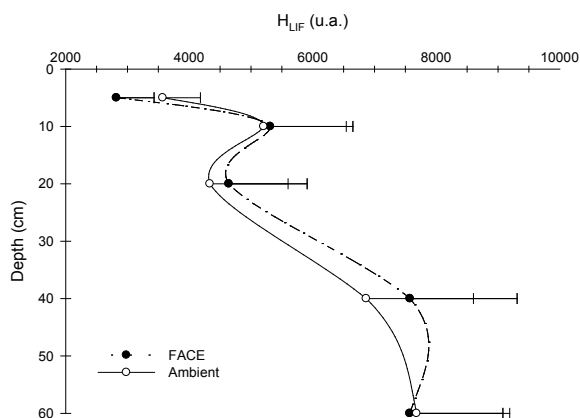

Figure 2 The humification index based on LIF spectroscopy (H$_{LIF}$) of soil organic matter as a function of CO$_2$ level in atmosphere in coffee growing area. Error bars = LSD (Least Significant Difference) of Student's t-test (p < 0.05). u.a.: means arbitrary units.

Decomposition of coffee leaves

Atmospheric CO$_2$ enrichment did not influence the decomposition rate of the coffee leaves and the C:N ratio of the remaining material (Table 3). The average degradation of vegetal material was 73% in a 360-day period. Initially the plant material had a C:N ratio of 17:1, at the end of the 360-day period this ratio was 10:1, regardless of enrichment or non-atmospheric CO$_2$. The N and C concentrations of the plant material in litterbag were also not influenced by atmospheric CO$_2$ enrichment.

Emissions of N$_2$O and CO$_2$

No differences were observed between treatments in accumulated emissions of N$_2$O and CO$_2$ during the period of two harvests (2013/2014

and 2014/2015) (Figure 3). These results confirm that the atmospheric enrichment with CO$_2$ did not influence the decomposition dynamics of organic materials added in the study area, and it is possible to conclude that the increase of the C and N stock observed previously is due to the increase of organic material deposition that the atmospheric enrichment of CO$_2$ provided.
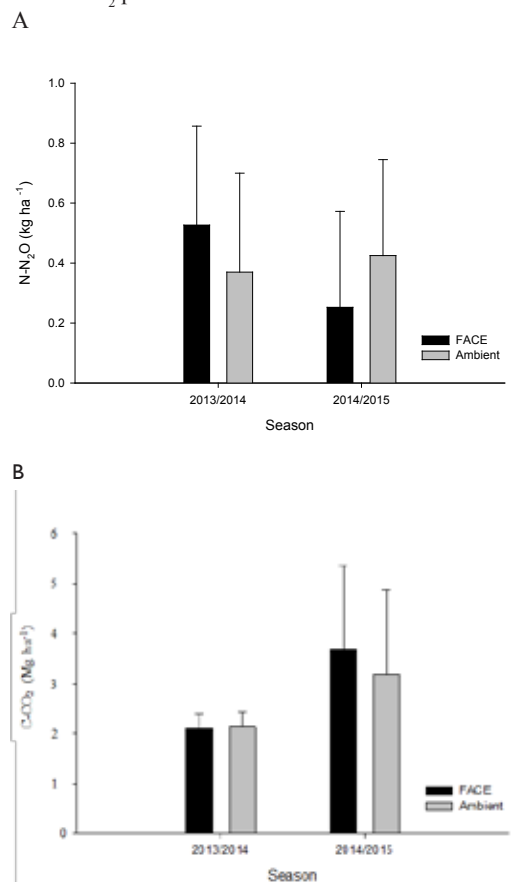

Figure 3 Accumulated emission of N-N$_2$O (A) e C-CO$_2$ (B) of soil in two harvests of coffee cultivated in an area with different levels of CO$_2$ atmospheric. Error bars = LSD (Least Significant Difference) of Student's t-test (p < 0.05).

Table 3 Decomposition of coffee leaves after harvesting, percentage of carbon and nitrogen and C:N ratio of remaining soil material as a function of CO$_2$ level in atmosphere in coffee growing area

Days	Dry Mass kg ha^{-1}		C %		N %		C:N ---	
	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]	FACE[1]	Ambient[2]
0	5000 a	5000 a	51.18 a	51.18 a	3.01 a	3.01 a	17.0 a	17.0 a
14	3868 a	3763 a	51.36 a	50.82 a	3.17 a	3.15 a	16.3 a	16.1 a
36	3325 a	3382 a	51.21 a	51.05 a	3.13 a	3.18 a	16.4 a	16.1 a
60	3030 a	2915 a	51.42 a	51.64 a	3.32 a	3.24 a	15.5 a	15.9 a
90	2733 a	2580 a	50.65 a	50.30 a	3.49 a	3.40 a	14.5 a	14.9 a
120	2925 a	3022 a	49.06 a	48.93 a	3.90 a	3.80 a	12.6 a	12.9 a
180	2139 a	2247 a	48.98 a	49.79 a	4.16 a	4.38 a	11.8 a	11.5 a
290	1473 a	1688 a	48.57 a	47.84 a	4.82 a	4.72 a	10.1 a	10.1 a
360	1348 a	1356 a	48.07 a	48.25 a	4.74 a	4.64 a	10.2 a	10.4 a

Averages followed by different letters in same line are statistically different by Student's t-test (p < 0.05)
[1]Treatment with atmospheric CO$_2$ enrichment, concentration of 550 µmol mol^{-1} of CO$_2$
[2]Treatment with ambient air, concentration of 390 µmol mol^{-1} of CO$_2$

Conclusion

After 43 months of experimentation, the atmospheric CO$_2$ enrichment in the area with coffee cultivation promoted an increase in soil C and N stocks at the first 5 cm of soil layer and this effect occurred due to the higher organic residue addition provided by coffee plants, once the decomposition process was not modified. Considering that the N$_2$O emission was not affected by atmospheric CO$_2$ enrichment, the conclusion is that the increase of this gas in atmosphere results in negative feedback for global warming due to the increase of soil sequestration potential of C in coffee grown area.

Acknowledgments

Conflicts of interests

Authors declare no conflict of interest exists.

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