



CO₂ and N₂O emissions in a soil chronosequence at a glacier retreat zone in Maritime Antarctica



A. Thomazini^{a,*}, E.S. Mendonça^a, D.B. Teixeira^b, I.C.C. Almeida^c, N. La Scala Jr.^b, L.P. Canellas^d, K.A. Spokas^e, D.M.B.P. Milori^f, C.V.G. Turbay^g, R.B.A. Fernandes^h, C.E.G.R. Schaefer^h

^a Department of Plant Production, Federal University of Espírito Santo, 29500-000 Alegre, Espírito Santo, Brazil

^b FCAV/UNESP, Via de Acesso, Prof. Paulo Donato Castellane s/n, 14884-900 Jaboticabal, SP, Brazil

^c Instituto Federal do Norte de Minas Gerais, Fazenda São Geraldo, s/n km. 06, 39480-000 Januária, Minas Gerais, Brazil

^d UENF – Universidade Estadual do Norte Fluminense Darcy Ribeiro, Núcleo de Desenvolvimento de Insumos Biológicos para a Agricultura (NUDIBA), Av. Alberto Lamego, 2000, Campos dos Goytacazes 28013-602, Rio de Janeiro, Brazil

^e USDA-ARS, Soil and Water Management Unit, University of Minnesota – St. Paul, MN 55108, USA

^f Embrapa Instrumentation Brazilian Agricultural Research Corporation, São Carlos, SP, Brazil

^g Department of Geology, Federal University of Espírito Santo, 29500-000 Alegre, Espírito Santo, Brazil

^h Universidade Federal de Viçosa, Departamento de Solos, Avenida P. H. Rolfs, s/n, 36570-000 Viçosa, Minas Gerais, Brazil

HIGHLIGHTS

- We evaluated soil organic matter and GHG emissions across a glacier retreat chronosequence.
- Soils exposed for a longer time increased soil organic matter and GHG emissions.
- Degree of humification in soil organic matter tended to be higher in newly exposed areas.
- The results would provide representative data for global warming effects.

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ABSTRACT

Studies of C cycle alterations are extremely important to identify changes due to climate change, especially in the polar ecosystem. The objectives of this study were to (i) examine patterns of soil CO₂-C and N₂O-N emissions, and (ii) evaluate the quantity and quality of soil organic matter across a glacier retreat chronosequence in the Maritime Antarctica. Field measurements were carried out during January and February 2010 (summer season) along a retreating zone of the White Eagle Glacier, at King George Island, Maritime Antarctica. Soil samples (0–10 cm) were collected along a 500-m transect at regular intervals to determine changes in soil organic matter. Field CO₂-C emission measurements and soil temperature were carried out at regular intervals. In addition, greenhouse gas production potentials were assessed through 100 days laboratory incubations. Soils exposed for a longer time tended to have greater concentrations of soluble salts and possess sandier textures. Total organic C (3.59 g kg⁻¹), total N (2.31 g kg⁻¹) and labile C (1.83 g kg⁻¹) tended to be lower near the glacier front compared with sites away from it, which is correlated with decreasing degree of humification of the soil organic matter with exposure time. Soil CO₂-C emissions tended to increase with distance from the glacier front. On average, the presence of vegetation increased CO₂-C emissions by 440%, or the equivalent of 0.633 g of CO₂-C m⁻² h⁻¹. Results suggest that newly exposed landsurfaces undergo soil formation with increasing labile C input from vegetation, accompanied by increasing soil CO₂-C emissions. Despite the importance of exposure time on CO₂-C production and emissions, there was no similar trend in soil N₂O-N production potentials as a function of glacial retreat. For N₂O, instead, the maximum production occurred in sites with the first stages of vegetation growth.

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* Corresponding author.

E-mail addresses: andre.thz@gmail.com (A. Thomazini), eduardo.mendonca@ufes.br (E.S. Mendonça), daniel.dbt@hotmail.com (D.B. Teixeira), ivancarreiro@yahoo.com.br (I.C.C. Almeida), lascalafca.unesp.br (N. La Scala), lucianocanellas@gmail.com (L.P. Canellas), kurt.spokas@ars.usda.gov (K.A. Spokas), deboramilori@embrapa.br (D.M.B.P. Milori), cturbay@gmail.com (C.V.G. Turbay), raphael@ufv.br (R.B.A. Fernandes), carlos.schaefer@ufv.br (C.E.G.R. Schaefer).

1. Introduction

The ecosystems of the Maritime Antarctica (between 61°00'–63°37' south, and 53°83'–62°83' west – The South Shetland Islands) are experiencing one of the most rapid localized trends of climate warming worldwide (Convey et al., 2011). Hence, it represents an important

climate sensitive proxy for responses expected in other more complex systems (Convey et al., 2011). Over the past 50 years the Antarctic Peninsula region has warmed by up to 3 °C, more than three times the global mean (Turner et al., 2009; Convey et al., 2011). Despite the extremely low temperatures and dry conditions, the soil environment holds a significant component of the seasonally unfrozen organic carbon reservoir (Burkins et al., 2001). Permafrost-affected soils (Gelisols) contain an estimated 393 Pg of C in the upper 100 cm (Bockheim and Hinkel, 2007), constituting nearly 25% of the global soil organic carbon pool (Lal and Kimble, 2000). Antarctic soils account for as much of 72% of the seasonally unfrozen and biologically available organic carbon, while lakes and streams account for 27 and 0.5%, respectively (Burkins et al., 2001). Soil organic carbon release can be an indicator of regional warming, since this carbon reservoir can be mineralized within relatively short periods (e.g., years versus centuries).

In recent decades, ice recession in the Antarctic Peninsula region has accelerated with global warming to rates that are unprecedented on a global scale (Kozieretska et al., 2010). A consequence of glacier recession is the exposure of formerly ice-covered landscapes to multiple new influences. These include environmental and biological factors, such as exposure to air, occupation by animals (primarily penguins), vegetation establishment, direct rainfall and more profound temperature changes (Simas et al., 2007; Schaefer et al., 2008; Mendonça et al., 2010; La Scala et al., 2010; Strauss et al., 2009; Convey et al., 2011). All these factors control soil formation (Jenny, 1946). One of the most significant soil influences is the penguin excreta accumulation and transformation in breeding places, which reacts with the underlying bedrock forming a layer of phosphorus-rich material, enhancing soil acidification, and plant development (Michel et al., 2006). Glacier recession may also affect surface albedo, biogeochemical weathering reactions, deposition of detritus, soil moisture and temperature fluctuations, and changes in microbial community compositions and activity (Gregorich et al., 2006; Hopkins et al., 2006; Schaefer et al., 2008; Strauss et al., 2009; Mendonça et al., 2010; Convey et al., 2011; Carvalho et al., 2012; Michel et al., 2012). It may result in changing soil respiration rates, affecting the production or consumption of greenhouse gases (GHG) at the glacier retreat zone, especially CO₂ and N₂O.

Along the Antarctica Peninsula, vegetation communities of native flowering plants found on the Antarctic continent (*Deschampsia antarctica* and *Colobanthus quitensis*) and cryptogams (bryophytes and lichens), have increased in size and number over the past 40 years (Smith, 2003; Kozieretska et al., 2010; Convey et al., 2011), partially as a response to glacial retreat (Strauss et al., 2009). These communities have received considerable research attention in recent years in the context of being indicators of biological responses to rapid environmental change (Parnikoza et al., 2009; Kozieretska et al., 2010) and the advanced pedogenetic processes (Simas et al., 2007; Schaefer et al., 2008; Almeida et al., 2014; Michel et al., 2014; Souza et al., 2014). However, vegetation development is highly variable at a glacier retreat zone and influenced by several soil physical (e.g., soil temperature, moisture, permafrost thawing) and biological factors (e.g., microbial community) (Mendonça et al., 2010; Almeida et al., 2014). Thus, alterations on permafrost and microbial communities may drive GHG emission to the atmosphere.

Antarctic soils are key environmental components determining ecosystem C and N cycling processes, such as primary production, decomposition and respiration (Mendonça et al., 2010; Cannone et al., 2012; Carvalho et al., 2012). Soil GHG emissions are influenced by climate changes via increasing temperatures, permafrost thawing, and soil moisture (Cannone et al., 2012; La Scala et al., 2010; Mendonça et al., 2010). The occurrence of vegetation increases the potential of the Antarctic soils to act as sink of atmospheric C, through its retention as organic C in the soil (Park et al., 2007; Cannone et al., 2012). Places with greater vegetation development tend to have greater total soil organic C and N, and GHG emissions (Simas et al., 2007; Carvalho et al., 2012; Vieira et al., 2013; Thomazini et al., 2014), than bare soil sites (La Scala

et al., 2010; Mendonça et al., 2010; Carvalho et al., 2012). Therefore, a large proportion of the C stored in soils is vulnerable for mineralization and subsequent CO₂-C release in the face of current global warming (La Scala et al., 2010). Changes in soil temperature could result in the reduction of the permafrost (Schaefer et al., 2008), increasing losses of C among ice-free soils.

Along a glacier retreat zone, the gradient of soil development, vegetation communities, soil moisture and temperature and soil organic matter may drive GHG and soil organic matter mineralization. Characterization of CO₂-C and N₂O-N emissions in Antarctic soils may help in establishing the relation between soil attributes and climatic changes scenarios along glacier retreat zones (Carvalho et al., 2012). Hence, we aimed to examine (i) patterns of soil CO₂-C and N₂O-N emissions and (ii) evaluate the quantity and quality of soil organic matter across a glacier retreat chronosequence in the Maritime Antarctica.

2. Material and methods

2.1. Site description

The study was carried out at new ice-free areas along the glacier retreat zone of White Eagle Glacier at Admiralty Bay, Low Head Peninsula, King George Island, South Shetland Islands (Fig. 1). There are no local meteorological stations located at Low head. For this reason, climatic data acquired at the Brazilian Commandant Ferraz, the nearest station to Low Head, where mean monthly air temperatures vary from −6.4 °C in July to +2.3 °C in February, and the mean annual precipitation is 400 mm. The mean annual air temperature was −1.1 and −2.6 °C for the years 2010 and 2011, respectively (Almeida et al., 2014). This air temperature and precipitation allows some plant growth, especially mosses, lichens and algae and the two higher plants *D. antarctica* and *C. quitensis* (Convey et al., 2011). Over the past 50 years, several studies have suggested that sea ice in Antarctica is actually decreasing (Gagné et al., 2015). Especially, the White Eagle Glacier front has retreated ~500 m since 1988, exposing soil and forming new ice-free areas (Piotr and Korczak, 2010). The glacier front is at the highest elevation (94 m above sea level) and has no vegetation and low pedogenetic development (Almeida et al., 2014). Permafrost occurs at a depth of 0.96 m (on the average). This zone shows intense frost heaving and cryoturbation during the summer months. The soil is skeletal and classified as a Turbic Haploturbel (Almeida et al., 2014), with a high proportion of coarse grains (>2 mm particles), including rock fragments (>4 mm). The glacial retreat is proceeding along the slope, with an older exposed site at lower elevation locations (29 m above the sea). Here, the parent material is till supplemented by the weathering of local basaltic rocks. When present, the vegetation cover is composed of a mixture of lichens and mosses (*Usnea* sp., *Sanionia uncinata*) and one higher plant (*D. antarctica*). The soil at this retreat zone is a Typic Haplogelepts (Almeida et al., 2014).

2.2. Soil sampling

The soil was sampled in January and February 2010 to determine (i) soil general properties, (ii) total soil organic carbon and total nitrogen, (iii) soil organic matter humification degree, (iv) GC/MS pyrolysis analyses, (v) laboratory GHG production potentials and (vi) microbial biomass carbon. Five soil samples were collected in three locations (hereafter named Sections 1, 2 and 3) at 0–10 and 10–20 cm depth. Section 1 was near the glacier front (from 0 to 150 m), Section 2 was an intermediate location (150 to 300 m from the glacier front) and Section 3 was the farthest point from the glacier front (300 to 500 m) (Fig. 1). The soil samples from the three sections were then thoroughly mixed to form a single homogeneous soil sample for each section and layer, air dried and passed through a 2 mm sieve to determine soil general properties (0–10 cm depth) and the degree of humification in soil organic matter (0–10 and 10–20 cm depth).

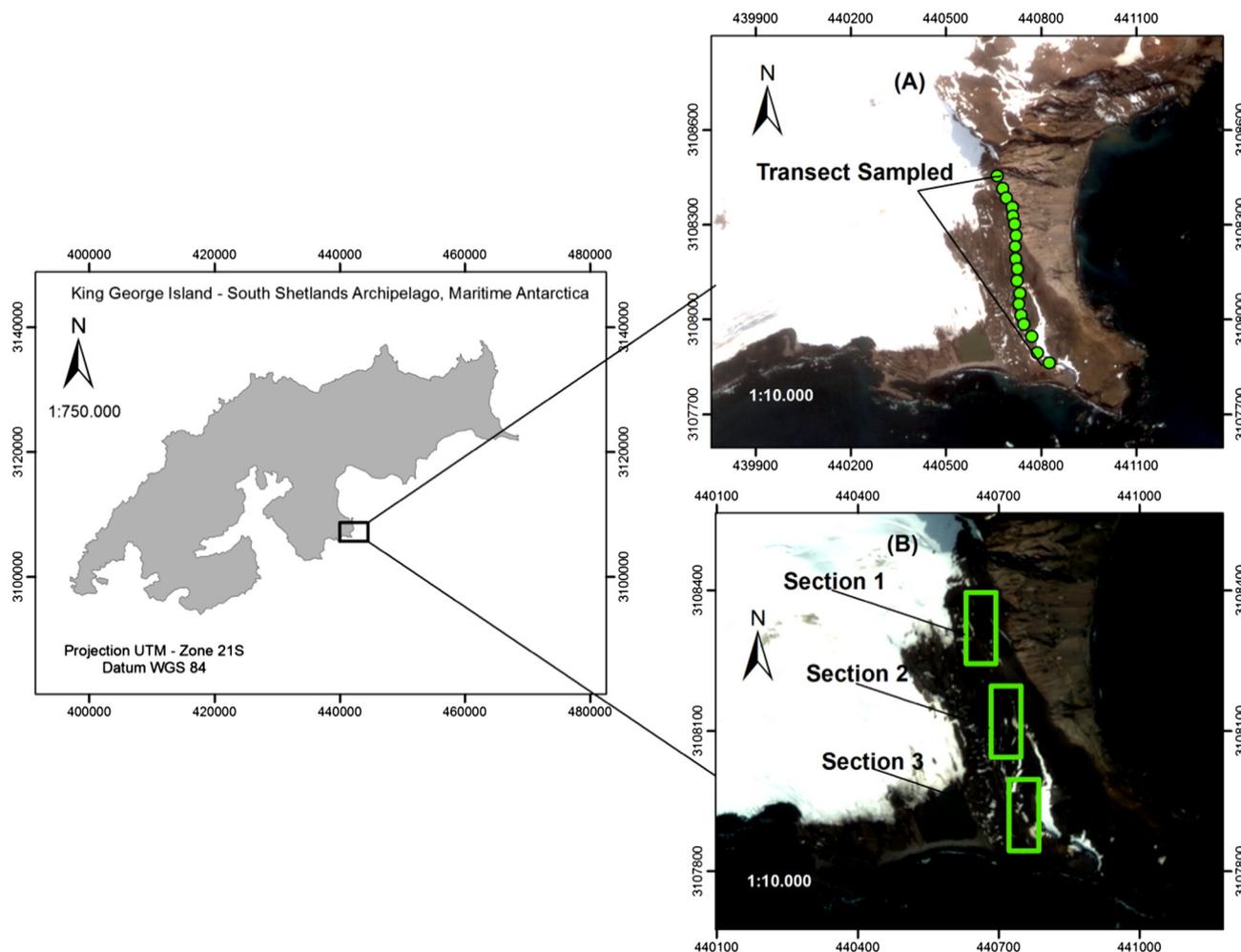


Fig. 1. Illustrative map showing the transect studied (A) and the sections (B) located at a glacier retreat zone in the White Eagle Glacier, King George Island, South Shetland Islands. The transect starts near the glacier front and ends 500 m away from it.

In addition, a sequence of soil samples were collected along a 500-m-long transect at 0–10 cm depth, at a regular interval of 25 m. Transects along glacier retreat fronts represent chronosequences, where distance from the glacier front corresponds to time since areas became ice-free (Strauss et al., 2009; Thomazini et al., 2014). The entire transect covers 500 m (away from the glacier front). At the 300 m point, soil samples with and without vegetation were collected at the same site, totaling eight soil samples with and eight soil samples without vegetation cover. These soil samples were air dried and passed through a sieve (2 mm) for GC/MS pyrolysis analyses. Soil subsamples of approximately 20 g were crushed in a mortar to pass a 250 μm mesh to determine total soil organic C, total N, labile C, and recalcitrant C. Fresh soil samples were taken, sieved through a 2 mm and stored at 4 $^{\circ}\text{C}$ until analyses. Fresh soil samples were used to determine laboratory GHG production potentials and microbial biomass carbon.

2.3. Soil general properties

Soil samples were analyzed at the soil laboratory at the Federal University of Espirito Santo, Agriculture Science Center. The pH was determined on a 1:5 soil:deionized water ratio; the potential acidity (H + Al) was extracted with $\text{Ca}(\text{OAc})_2$ 0.5 mol L^{-1} buffered to pH 7.0, and quantified by titration with NaOH 0.0606 mol L^{-1} . Exchangeable Ca^{2+} , Mg^{2+} and Al^{3+} were extracted with 1 mol L^{-1} KCl and Na^{+} and K^{+} were extracted with Melich-1 (Embrapa, 1997). The element content in the extracts was determined by atomic absorption (Ca^{2+} , Mg^{2+} and Al^{3+}), flame emission (Na^{+} and K^{+}) and photocolometry (P). The effective

cation exchange capacity (CECE) was calculated by the sum of cations (Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} and Al^{3+}) and total cation exchange capacity (CTCT) estimated by the sum of bases and potential acidity. The particle size analyses was performed by the pipette method (Embrapa, 1997).

2.4. Degree of humification in soil organic matter

Laser-Induced Fluorescence Spectroscopy (LIFS) of the soil samples was used to assess the degree of humification in soil organic matter. Homogenized soil samples were used to produce pellets, prepared with a hydraulic press using approximately 0.5 g of soil. The pellets were approximately 2×10 mm. The ratio of the area under this fluorescence emission per total organic C content (g kg^{-1}) was defined as the soil organic matter humification index (HLIF) and is expressed in arbitrary units (Milori et al., 2006). Samples were excited with 458 nm blue radiation, emitted by argon laser equipment (Coherent Innova 90-6, Coherent Inc., Santa Clara, CA) with a 400 mW power. A prism was placed in front of the laser exit to remove background gas fluorescence. The back scattering fluorescence emitted by excited samples was collected through a convergent lens and focused on the slit of a monochromator (focal distance of 240 mm, 1200 g mm^{-1} and blaze in 500 nm-CVI). Signals were multiplied by a Hamamatsu photomultiplier (Hamamatsu, Hamamatsu City, Japan), adjusted to the maximum sensitivity in the visible region (530 nm), and filtered and amplified by a lock-in amplifier. The system functioning and the data acquisition were controlled through customized software. The spectral resolution was 3 nm (Milori et al., 2006).

2.5. GC/MS pyrolysis analyses

A dried soil sample (2 g) was placed in a quartz boat and moistened with 3.0 mL of tetramethylammonium hydroxide – TMAH (25% in methanol) solution. After drying the mixture under a gentle stream of nitrogen for about 10 min, the sample was introduced into a Pyrex tubular reactor (50 cm × 3.5 cm i.d.) and heated at 400 °C for 30 min (Barnstead Thermolyne 21100 furnace). The thermally released products were continuously transferred by a flow of helium (20 mL min⁻¹) into two successive chloroform (50 mL) traps kept in ice/salt baths. The chloroform solutions were combined in a round flask and concentrated by rotoevaporation. The residue was redissolved in 1 mL of chloroform and transferred to a glass vial for GC-MS analyses. Three thermochemolysis replicates were carried out for each soil sample.

The products of pyrolysis were analyzed by GC-MS. GC separations were carried out with a GCMS QP2010 Plus instrument (Shimadzu, Tokyo, Japan) equipped with an Rtx-5MS WCOT capillary column (Restek, 30 m × 0.25 mm; film thickness = 0.25 μm). Chromatographic separation was achieved with the following temperature program: 60 °C for 1 min (isothermal), raised at 7 °C min⁻¹ to 100 °C and then at 4 °C min⁻¹ to 320 °C followed by 10 min at 320 °C (isothermal). Helium was the carrier gas at 1.90 mL min⁻¹, the injector temperature was 250 °C, and the split injection mode had a split flow at 30 mL min⁻¹. Mass spectra were obtained in EI mode (70 eV), scanning in the range of m/z 45–850 with a cycle time of 1 s. Compound identification was based on comparison of mass spectra with the NIST library database, published spectra, and neat standards. For quantitative analyses, due to the large variety of detected compounds with different chromatographic responses, external calibration curves were built by mixing methyl esters and/or methyl ethers of the following molecular standards: tridecanoic acid, octadecanol, 16-hydroxyhexadecanoic acid, docosanoic acid, β-sitosterol, and cinnamic acid. Increasing amounts of standard mixtures were placed in a quartz boat and moistened with 0.5 mL of TMAH (25% in methanol) solution. The same pyrolysis conditions as for soil samples were applied to the analytical standards.

2.6. Total soil organic carbon and total nitrogen

Total soil organic C was determined by wet oxidation with K₂Cr₂O₇ 0.167 mol L⁻¹ in the presence of sulfuric acid with external heating (Yeomans and Bremner, 1988). Total N was determined by sulfuric acid digestion followed by Kjeldahl distillation (Bremner, 1982; Tedesco et al., 1995). The fractions of soil organic C were estimated through a modified Walkley and Black method as described by Chan et al. (2001) using 2.5, 5 and 10 mL of concentrated H₂SO₄ that resulted in three acid–aqueous solution ratios of 0.25:1, 0.5:1 and 1:1 (which corresponded, respectively to 3, 6 and 9 mol L⁻¹ H₂SO₄). The amount of soil organic C determined using 2.5, 5 and 10 mL of concentrated H₂SO₄ when compared with total C, allowed the separation of total C into the following four fractions of decreasing oxidizability: Fraction I (very labile) organic C oxidizable under 3 mol L⁻¹ H₂SO₄; Fraction II (labile) the difference in soil organic C extracted between 6 and 3 mol L⁻¹ H₂SO₄; Fraction III (less labile) the difference in soil organic C extracted between 9 and 6 mol L⁻¹ H₂SO₄; and Fraction IV (non-labile) residual organic C after reaction with 9 mol L⁻¹ H₂SO₄ when compared with total C. The sum of fractions I and II was considered as the labile C and the sum of fractions III and IV as the recalcitrant C (Chan et al., 2001). The Labile/recalcitrant C ratio was calculated by the ratio between labile C and recalcitrant C. C/N ratio was calculated by the ratio between total organic C and total N.

2.7. Field soil CO₂-C emission and soil temperature

Soil CO₂-C emission (from the respiration of microorganisms, plant roots and shoots) and soil temperature (5 cm) were performed along a 500-m-long transect at 0–0.5 cm depth, at a regular interval of 25 m,

totaling 21 sites with three replicates at each site. The transect started 500 m away from the glacier front and ended at the glacier front (0). Whenever possible, soil CO₂-C emission and soil temperature that were taken in paired vegetated and non-vegetated sites at each location were collected. Soil CO₂ emissions (μmol m⁻² s⁻¹) were measured using the LI-8100 portable analyzer (Li-Cor, USA) coupled to a dynamic chamber. The CO₂ rates were measured by an infrared gas analyzer system that quantifies concentration through optical absorption spectroscopy. The LI-8100 portable analyzer was calibrated at the factory using precision gases (CO₂ and H₂O gas standards) at controlled temperatures. The soil chamber has an internal volume of 854.2 cm³ and a circular contact area with the soil of 83.7 cm². PVC soil collars (0.10 m diameter × cm high) were previously placed (5 cm) at each site (24 h prior to measurement). Measurements of CO₂ emissions at each survey point were based on three measurements over 1.5 min, during which time measurements were made of CO₂ concentrations inside the chamber at 3 s intervals. At the same time, soil temperature (°C) measurements (DELTA, model DT 625, Brazil) were made at 5 cm depth for all sites.

2.8. Laboratory GHG production potentials and microbial biomass carbon

Soil CO₂-C and N₂O-N production potentials were determined by following an incubation method at field capacity (–33 kPa) and controlled soil temperature (22 °C ± 1 °C) (Spokas and Reicosky, 2009). CO₂-C and N₂O-N production potentials were evaluated on a gas chromatographic-mass spectrometer (GC-MS) system to quantify gas production over the 100-d incubation period. Triplicate sub-samples (5 g of soil each one) were placed in three sterilized 125 mL serum vials (Wheaton Glass, Millville, NJ) and sealed with red butyl rubber septa (Grace, Deerfield, IL). Control incubations were run as the incubation blanks to ensure that no sorption or reaction of the analyzed gases with the serum vial or septa occurred. If the O₂ level dropped below 15% (v/v) during the incubation, the incubation was terminated and the rates of production were calculated up to this point as the linear fit of accumulation of CO₂ and N₂O in the headspace with time to maintain comparison of aerobic conditions across all incubations. An initial 7 day period was allowed for the soil to equilibrate after rewetting (Franzluebbers et al., 1996; Fierer and Schimel, 2003). Microbial biomass C was estimated through the glucose amendment method proposed by Anderson and Domsch (1978), where 1 μL CO₂ h⁻¹ equals 40 mg of microbial biomass after optimized glucose additions.

2.9. Data analyses

Soil general properties and the degree of humification in soil organic matter were interpreted based on general trends of the replicate means along the glacier retreat zone. Kruskal–Wallis test was performed to test for differences of total soil organic C, total N, labile C, recalcitrant C, microbial biomass C, labile/recalcitrant C ratio, C/N ratio, field soil CO₂-C emission and soil temperature, laboratory GHG production potentials and between sites with and without vegetation cover (Siegel and Castellan, 1988). A probability of *p* < 0.05 was used to determine the statistical significance. Spearman's rank correlation was performed between soil CO₂-C and N₂O-N emissions (in situ and lab) with soil temperature along the transect.

Two separate principal component analyses (PCA) were performed. The GC/MS pyrolysis dataset consisted of a matrix (21 × 115) where each row represents one of the soil samples analyzed. The variables were the chromatographic areas and their retention times. The GC/MS pyrolysis dataset was auto-scaled and the PCA was performed using the statistical software package The Unscrambler × 10.1 (Camo Inc., Oslo, Norway). In addition, total soil organic C, total N, labile C, recalcitrant C, microbial biomass C, labile/recalcitrant C ratio, C/N ratio, field soil CO₂-C emission, soil temperature and laboratory GHG production potentials were also subjected to PCA. A multivariate analyses was

performed to establish whether compounds described by spectral areas and soil attributes could be separated according to geographical position along the transect.

3. Results

3.1. Soil general properties

Soil general properties along the transect are presented in Table 1. Soil samples showed increasing salinity and sand content with greater distance from the glacier front (Table 1). In addition, P, K⁺, Na⁺, Al³⁺ availability and cation exchange capacity values generally followed this same trend (Table 1). Acidic soils were observed in Section 3 with potential acidity (3.33 cmol_c dm⁻³). Also, clay amounts (a weathering index) were higher in Section 3 (207 g kg⁻¹), while near the glacier front showed a lower clay amount (71 g kg⁻¹). Sandy texture was more abundant near glacier's edge compared with the other locations (Table 1).

3.2. Degree of humification in soil organic matter

Mean values of the degree of humification in soil organic matter along the transect sampled are illustrated in Fig. 2. The degree of humification in soil organic matter tended to increase with depth and decrease with distance from the glacier front. The effects of vegetation communities on the degree of humification in soil organic matter are presented in Table 2. Sites with vegetation tended to have lower degree of humification in soil organic matter compared to sites without vegetation.

3.3. GC/MS pyrolysis analyses

Soil samples were separated on principal component analyses (PCA) according to their chemical nature (Fig. 3). Soil samples with longer environmental exposition time and with vegetation cover, had derivative lignin compounds, normal alcohol distribution with dodecanol, sixteen different alkanes and hexacosane (Fig. 3, Group 2). Hexanedioic acid, bis(2-ethylhexyl) ester had the highest loading coefficient in the PCA analyses (0.89). These samples, with and without vegetation occurrence, also had carbohydrate derivatives, nitrogen compounds, carbohydrates, and two aromatic compounds with retention times at 29.61 and 32.27 min identified as 1,2,3,4-tetramethylnaphthalene. On the other hand, samples closer to the glacier front (without vegetation) tended to have methylated fatty acids, including tricosanoic and tetradecanoic acids, which were not observed in samples with vegetation distance from the glacier front (Fig. 3, Group 1). Furthermore, steroids and terpenes were found only in the newly exposed soils, closer to the glacier front.

3.4. Total soil organic carbon, total nitrogen and microbial biomass carbon

Mean values of total organic C, total N, labile C, recalcitrant C and microbial biomass C along the chronosequence are shown in Fig. 4. Distance from the glacier front impacted general soil organic matter parameters. Total organic C, total N, labile C, recalcitrant C, microbial biomass C and

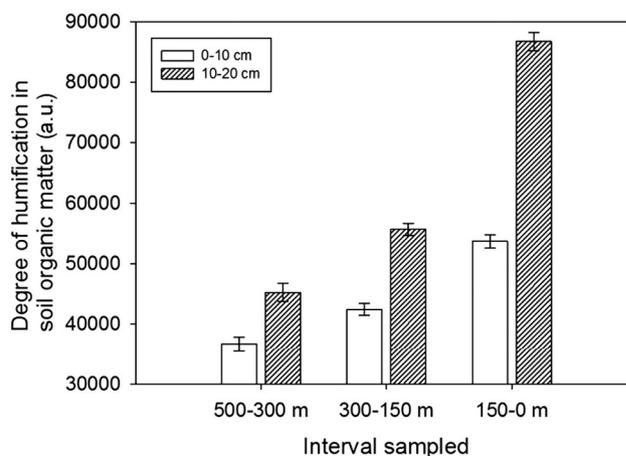


Fig. 2. Degree of humification in soil organic matter along the transect sampled at two soil layers. Section 1 was near the glacier front (from 0 to 150 m), Section 2 was an intermediate location (150 to 300 m from the glacier front) and Section 3 was the farthest point from the glacier front (300 to 500 m); a.u.: arbitrary units.

labile/recalcitrant C ratio increased with distance from the glacier front (Fig. 4). There is an occurrence of discontinuous vegetation communities in sites away from the glacier front. Significantly higher ($p < 0.05$, Kruskal–Wallis test) total organic C, total N, labile C, recalcitrant C and microbial biomass C were recorded in sites with vegetation (on the average: 14.08; 16.21; 12.85; 9.48 g kg⁻¹ and 155.53 μg g⁻¹, respectively) in comparison with sites without vegetation (on the average: 3.59; 2.31; 1.83; 3.94 g kg⁻¹ and 77.39 μg g⁻¹, respectively). C/N ratio was significantly lower ($p < 0.05$, Kruskal–Wallis test) in vegetated sites. Two principal components (PC1 and PC2) explained 58.17 and 56.90% of the variance in the data set, for vegetated and non-vegetated sites, respectively (Table 3). Through PCA, soil samples along the transect were separated in the bi-plot diagram (Fig. 5). In vegetated sites, PC1 had two highly weighted variables: microbial biomass C and labile/recalcitrant C ratio and PC1 had one highly weighted variable: labile C. In non-vegetated sites, PC1 had three highly weighted variables: total organic C, microbial biomass C and CO₂-C production potential. The highly weighted variables for the PC2 included labile C and C/N ratio.

3.5. Field CO₂-C emission and soil temperature

Field soil CO₂-C emissions and soil temperature along the sequence are presented in Fig. 6. Soil CO₂-C emissions ranged from 0 to 2.55 μmol m⁻² s⁻¹ along the glacier retreat zone. Significantly higher ($p < 0.05$, Kruskal–Wallis test) soil CO₂-C emissions were recorded in sites with vegetation (1.03 μmol m⁻² s⁻¹ in average) compared with non-vegetated sites (0.19 μmol m⁻² s⁻¹ in average). Average soil temperature followed the same pattern being 3.4 °C in sites with vegetation and 3.2 °C without vegetation. Despite expectations, soil temperature did not differ between vegetated and non-vegetated sites ($p = 0.585$, Kruskal–Wallis test).

Table 1

Soil general properties (0–10 cm) along the transect sampled at the glacier retreat zone.

Section	pH	P				Ca		Al	Al + H	CEC _E	CEC _T	Sand	Clay
		P	K	Na	Mg	Ca							
		mg kg ⁻¹				cmol _c kg ⁻¹							
1	6.0	232	103	232	2.26	9.73	0.00	0.00	13.30	13.30	766	71	
2	6.9	201	111	317	2.51	9.26	0.00	0.00	13.40	13.40	532	116	
3	5.0	1069	389	393	3.38	8.85	0.24	3.33	15.20	18.30	519	207	

pH: active acidity; P: phosphorus; K: potassium; Na: sodium; Ca: calcium; Mg: magnesium; Al: aluminium; H + Al: potential acidity; CEC_E: effective cation exchange capacity; CEC_T: total cation exchange capacity; Section 1 was near the glacier (from 0 to 150 m), Section 2 was an intermediate location (150 to 300 m from the glacier front) and Section 3 was the farthest point from the glacier front (300 to 500 m).

Table 2
Effects of vegetation communities on degree of humification in soil organic matter along the transect sampled at two soil layers.

Degree of humification in soil organic matter (a.u.)		
Soil layer (cm)	With vegetation	Without vegetation
0–10 cm	(37 ± 1) 10 ³ n = 8;	(40.4 ± 0.9) 10 ³ n = 10;
10–20 cm	(45 ± 2) 10 ³ n = 3;	(74 ± 1) 10 ³ n = 4;

n = number of replicates; a.u.: arbitrary units.

3.6. Laboratory GHG production potentials

Similar to the observations of the surface CO₂-C emissions, significantly higher ($p < 0.05$, Kruskal–Wallis test) CO₂-C production potentials were observed in vegetated sites (2.62 µg C/g soil/day) than in non-vegetated sites (1.10 µg C/g soil/day) (Fig. 5). On the other hand, N₂O-N production potentials did not differ among vegetated and non-vegetated sites ($p = 0.632$, Kruskal–Wallis test) (Fig. 6). CO₂-C field emissions were negatively correlated to soil temperature in vegetated sites ($r = -0.631$; $p = 0.028$, Spearman's rank correlation). However, CO₂-C incubations and temperature were negatively correlated in vegetated sites ($r = -0.521$, $p = 0.097$, Spearman's rank correlation), but no correlation was observed in non-vegetated sites ($r = 0.052$, $p = 0.891$, Spearman's rank correlation).

4. Discussion

4.1. Soil general properties

Soil chemical, physical attributes and organic matter changed with distance from the glacier front. Results suggest that soils along the chronosequence tended to have greater salinity, pH, potassium and phosphorus contents with increasing distance from the glacier front. Compared with the newly exposed glacial zones (Section 1), soil samples at the end of transect sampled probably have been exposed for several hundred years and influenced by penguin and bird rookeries in the past (Simas et al., 2007; Thomazini et al., 2014). Therefore, these soils have a greater soil development. This is related to the intensive seasonal input of nutrient-rich organic material by bird droppings during the summer, leading to the formation of ornithogenic soils (Tatur et al., 1997; Simas et al., 2007).

High guano inputs in former sites away from the glacier front, create an acid environment with low pH values (Michel et al., 2006; Simas

et al., 2007). These sites become progressively less acid with additional soil development, when the sites are abandoned and fresh guano input ceases (Michel et al., 2006). This is mainly explained by mineral weathering and high amounts of organic carbon that can neutralize part of the acidity at former sites, resulting in a more buffered soil (Michel et al., 2006; Carvalho et al., 2013). Former sites are also related to high amounts of exchangeable Ca²⁺, Mg²⁺, K⁺ and phosphorus (Simas et al., 2007). These sites with moderate to high abundance of nutrients show more diverse vegetation than freshly exposed sites. With glacial retreat, warmer soil temperatures and higher water availability result in deeper microbial active soil layers and promote mineral weathering, which also supports vegetation development (Campbell and Claridge, 1987).

4.2. Degree of humification in soil organic matter

Results show that the degree of humification in soil organic matter tended to be lower at the surface, increasing with depth (Fig. 2). At the topsoil, the intense input of fresh organic material from plants may decrease soil humification degree, since this material is typically more labile and therefore less aromatic in character. On the other hand, organic matter found at depth has been incorporated into the soil as more recalcitrant forms (more resistant to mineralization). This could be related to intense cryoturbation of these soils, and the incipient podsolization process, by which organic material is moved to deeper layers, where stabilization occurs (Michel et al., 2006; Simas et al., 2007). Amino compounds have an important role in the humification process (Carvalho et al., 2013), since these compounds participate in the condensation of sugar-amine compounds and reactions between quinones and amino acids (Beyer et al., 1995).

4.3. GC/MS pyrolysis analyses

Pyrolysis analyses showed that these soils tended to have a fibric nature and low amount of aromatic compounds. Most of these compounds are biodegradable, predominant non-lignin tissues from lower plants. This is in agreement with the results of Michel et al. (2006) and Carvalho et al. (2013). Basically, the organic matter consists of non-aromatic compounds, with aliphatic structures and proteins (Beyer et al., 1995). Despite being fairly low complexity compounds, which normally would be mineralized, these organic compounds have longer than expected preservation, probably due to the low soil microbial activity (Fig. 4) and slow organic matter decomposition rates imposed by the environment (Beyer et al., 1995; Michel et al., 2006; Carvalho et al., 2013). This leads to organic matter preservation of readily degradable C for longer periods, provided soil temperatures do not increase leading to altering these organic C dynamics. Therefore, the soil organic C further away from the glacier front is more at risk of mineralization. PCA (Fig. 3) showed that according to the chemical nature, the group 2 formed in the diagram with soil samples away from the glacier front, is generally characterized by greater fragility (higher lability) than the group 1 near the glacier front. This is consistent with results of humification degree, which show more labile organic matter in sites away from the glacier front due to inputs of fresh organic matter from the vegetation.

4.4. Total soil organic carbon, total nitrogen and microbial biomass carbon

Total soil organic C, total N, labile C, recalcitrant C, microbial biomass C and labile/recalcitrant C ratio were greater away from the glacier front, and decreased with increasing proximity to the glacier. This is consistent with pedogenesis (time factor), since these areas are longer exposed and have greater vegetation establishment (Thomazini et al., 2014). Hence, increases in the general soil organic matter parameters with distance from the glacier front are probably explained by a corresponding increase in soil development (La Scala et al., 2010; Mendonça et al., 2010; Cannone

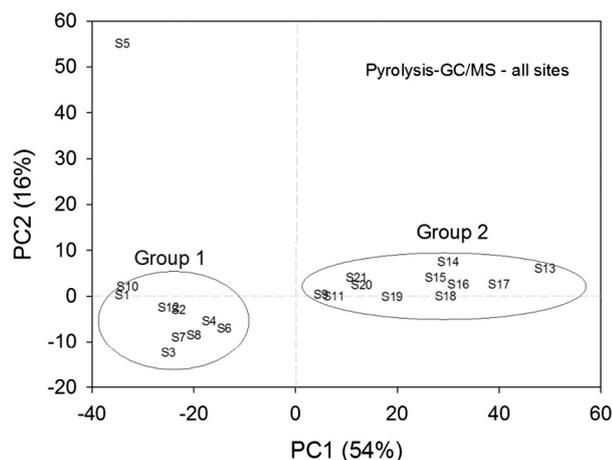


Fig. 3. PCA indicating good separation of soil samples in different groups according to geographical location along the chronosequence. The transect starts collecting soil sample 1 (S1) near the glacier front and ends in 21 (S21), away from the glacier front.

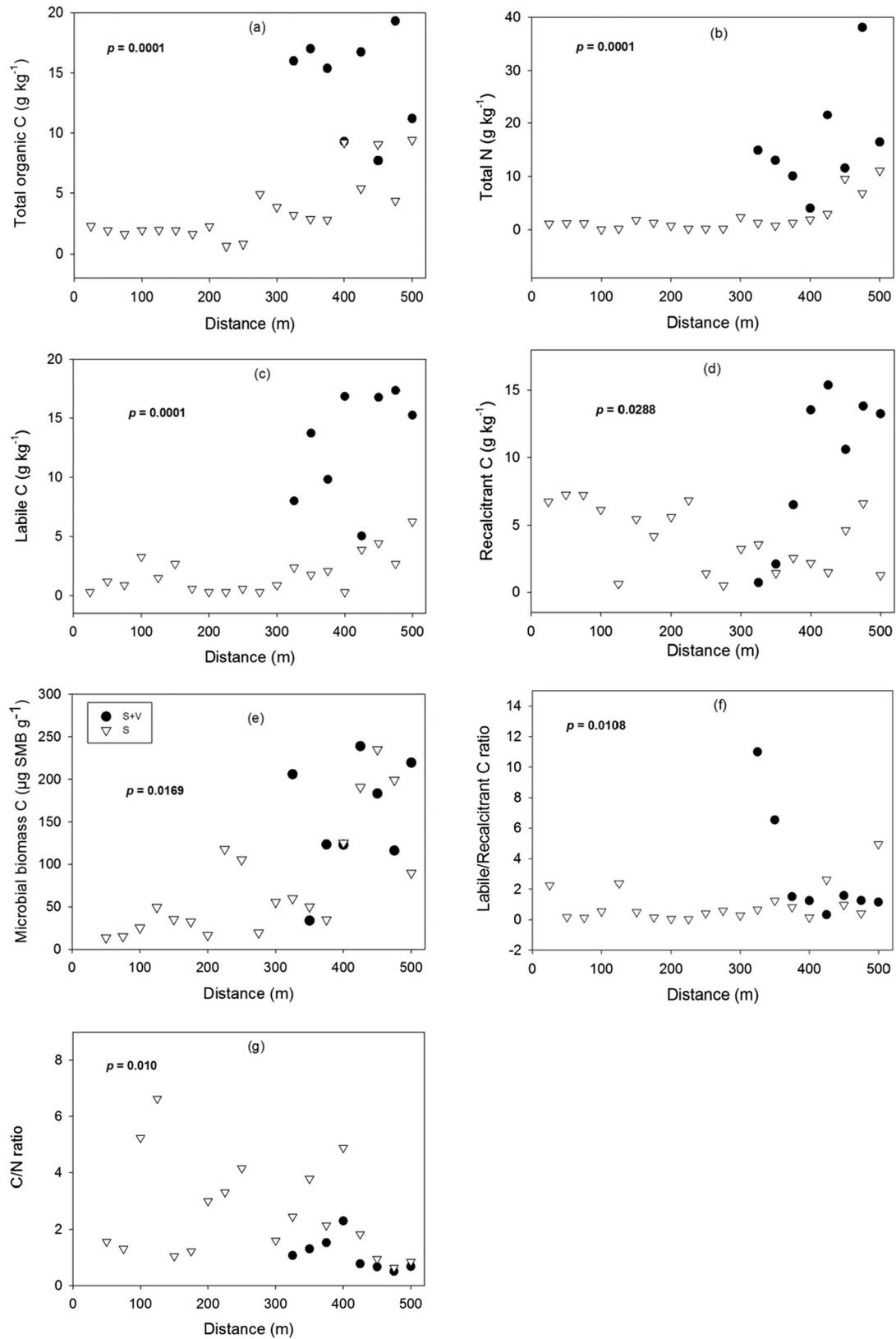


Fig 4. Mean values of total organic C (a), total N (b), labile C (c), recalcitrant C (d), microbial biomass C (e), labile/recalcitrant C ratio (f) and C/N ratio (g) along the transect at the glacier retreat zone, at 0–10 cm depth. The transect starts near the glacier front and ends 500 m away from it. Notes: S = soil without vegetation; and S + V = soil with vegetation. p -values are derived using the Kruskal–Wallis test and give significant differences between sites with and without vegetation cover in the case of $p < 0.05$.

et al., 2012). With longer time of exposure, higher is the input of C in the soil by organisms such as lichens, grasses, birds, penguins and soil microbiota (Tatur et al., 1997; Simas et al., 2007; Mendonça et al., 2010;

Cannone et al., 2012). This, in turn, favors the soil formation and organic C accumulation (Michel et al., 2006; Cannone et al., 2012). Generally, sites with well developed vegetation communities tend to have greater

Table 3
Outcome of principal component analyses for the first two principal components (PCs).

	Vegetated sites		Non-vegetated sites	
	PC1	PC2	PC1	PC2
Principal components	PC1	PC2	PC1	PC2
Eigenvalue	4.06	2.34	4.06	2.20
Variability (%)	36.89	21.28	36.95	19.96
Cumulative (%)	36.89	58.17	36.95	56.90
% explained by each variable:				
Soil CO ₂ -C emissions (in situ)	2.50	3.37	4.75	1.25
Soil temperature	12.99	5.69	0.14	1.15
Total organic C	0.00	4.52	16.55	0.45
Microbial biomass C	16.02	11.45	17.07	0.73
Recalcitrant C	12.28	14.05	3.74	14.28
Labile C	1.58	26.13	7.61	21.38
Total N	8.37	5.83	13.10	13.20
CO ₂ -C production (lab)	13.81	9.28	15.98	5.05
N ₂ O-N production (lab)	13.82	5.02	10.38	14.24
Labile/recalcitrant C ratio	15.01	3.75	7.76	0.43
C/N ratio	3.63	10.90	2.92	27.84

Boldface variables are considered highly weighted.

total soil organic C and total N than sites without vegetation (Park et al., 2007). In sites near the glacier, erosion is intense and soils are less developed and have lower soil organic matter (Carvalho et al., 2012). Michel et al. (2006) reported soil organic C in Antarctic soils ranging from 10 to 140 g kg⁻¹. Simas et al. (2007) showed that at the surface, high organic matter accumulation forms dark brown umbric epipedons and in poorly drained areas, part of the organic matter is preserved within the permafrost. Since the organic C preservation is highly dependent on soil temperatures, long-term increases in air temperatures will decrease the background organic C reservoir of Antarctica soils (Mendonça et al., 2010; Michel et al., 2012). According to the PCA, the well formed groups in the bi-plot diagram (Fig. 5) are directly related to the variables related to soil organic matter status and vegetation appearance (labile C input) in the glacier retreat zone. There is a trend of higher labile/recalcitrant C ratio that is confronted with lower degree of humification in soil organic matter in soil samples away from the glacier. This is also demonstrated in the GC/MS pyrolysis analysis, where compounds identified in soil samples away from the glacier are more sensitive to mineralization.

4.5. Field CO₂-C emissions, soil temperature and laboratory GHG production potentials

The results of soil organic matter are consistent with progressively greater soil CO₂-C emissions away from the glacier front. This is mainly related to plant respiration, contributing to the total ecosystem respiration

(Thomazini et al., 2014). However, CO₂-C incubations showed that even without plant respiration contribution, significantly higher ($p < 0.05$, Kruskal–Wallis test) CO₂-C emissions were found away from the glacier front, compared to sites near the glacier. Soil temperature did not differ ($p > 0.05$, Kruskal–Wallis test) between vegetated and non-vegetated sites at a glacier retreat zone. However, a slight decrease was observed near the glacier, probably due to glacial melting. The soil CO₂-C emissions from most global soil environments are considered a measure of both microbial respiration and root respiration (Davidson and Janssens, 2006; La Scala et al., 2010; Mendonça et al., 2010; Kuzyakov and Gavrichkova, 2010; Cannone et al., 2012). Root and aerial parts of plants can greatly contribute to the total soil respiration (Mendonça et al., 2010; Cannone et al., 2012). In the Antarctic environment, variability of soil CO₂-C emissions depends almost exclusively on soil temperature and water content (La Scala et al., 2010), including plant respiration on total ecosystem respiration (Cannone et al., 2012). Results are consistent with those of La Scala et al. (2010), who reported CO₂-C emissions 514% higher under vegetated sites than at bare sites. These values correspond to 0.162 g of CO₂-C m⁻² h⁻¹ at vegetated sites and 0.026 g of CO₂-C m⁻² h⁻¹ at bare soil. Carvalho et al. (2012) reported mean CO₂-C emissions varying from 0.034 to 0.472 g of CO₂-C m⁻² h⁻¹ barren soil and from 0.145 to 1.352 g of CO₂-C m⁻² h⁻¹ for vegetated soil.

Results show an important contribution of CO₂-C emissions from microbial activity, which increases with distance from the glacier (Fig. 4e). Microbial activity and soil organic carbon mineralization will affect net CO₂-C fluxes from the soil (in vegetated and non-vegetated soils). However, we did not evaluate the C sequestration potential of the plants, which may alter the C balance of these areas. Vegetation may increase the potential of the soils to act as sink of atmospheric C, through its deposition of organic C materials and root exudates (Michel et al., 2006; Mendonça et al., 2010; La Scala et al., 2010). However, Cannone et al. (2012) reported that these soils have higher rates of soil respiration and organic matter decomposition than photosynthesis, conversely, resulting in positive net ecosystem exchange, acting as a source of C to the atmosphere. This was also observed in the current study, where the vegetated soil typically had higher C contents and greater CO₂ emissions.

N₂O-N emissions showed different patterns compared to the CO₂-C emissions and other soil properties. The current study reported a slight increase in N₂O-N emissions away from the glacier. N₂O-N emissions did not appear to be strongly affected by vegetation cover by location, where total N is significantly higher ($p < 0.05$, Kruskal–Wallis test) at a glacier retreat zone. Thus, the mineral N contents had no significantly effect on the fluxes of N₂O-N in the current study. It is possible since results showed no statistical differences ($p > 0.05$, Kruskal–Wallis test) between vegetated and non-vegetated sites related to N₂O-N emissions.

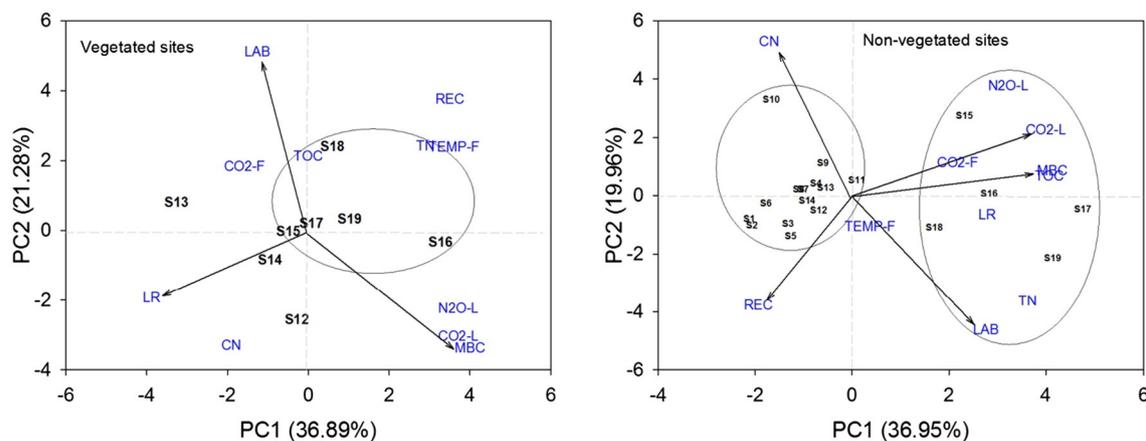


Fig. 5. Bi-plot diagram from the PCA of soil attributes along the transect. The transect starts collecting soil sample 1 (S1) near the glacier front and ends in S19 away from the glacier front. CO₂-F: Soil CO₂-C emissions (in situ), TEM-F: Soil temperature; TOC: Total organic C; MBC: Microbial biomass C; REC: Recalcitrant C; LAB: Labile C; TN: Total N; CO₂-L: CO₂-C production potentials; N₂O-L: N₂O-N production potentials; LR: Labile/Recalcitrant C ratio; CN: C/N ratio.

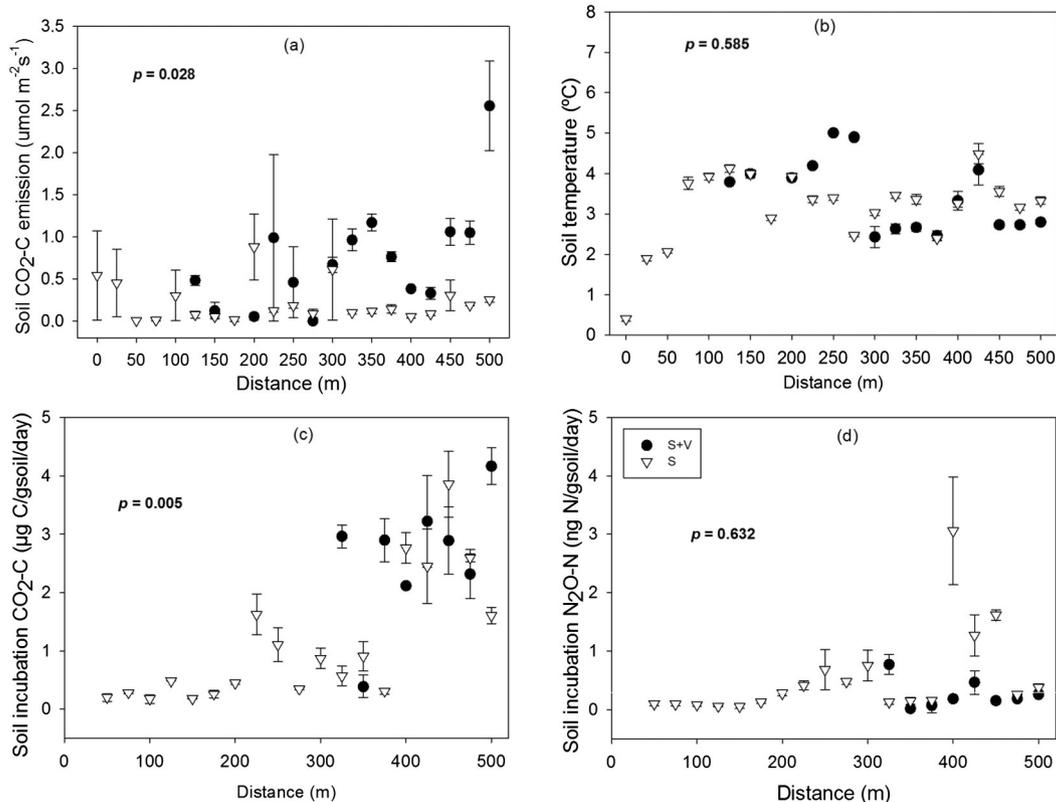


Fig. 6. Soil CO₂-C emissions (a) soil temperature in the field (b) and CO₂-C (c) and N₂O-N incubations (d) data along the glacier retreat zone. The transect starts in 500 m (away from the glacier front) and ends in 0 (near the glacier front). S = soil without vegetation; S + V = soil with vegetation. Vertical bars represent the standard error. *p*-values are derived using the Kruskal–Wallis test and give significant differences between sites with and without vegetation cover in the case of *p* < 0.05.

This is contrary to Vieira et al. (2013), who observed higher N₂O-N emissions rates in the soil under the presence of vegetation and bird activity. Strauss et al. (2009) also demonstrated that N contents increased with distance from the glacier. Possibly, variations of soil pH and soil aeration are potential factors. In this study, newly exposed sites are the most aerated soils, with sandy texture, which may decrease N₂O-N emission mineralization rate than the corresponding paired bare soil sample. Oxygen availability is an important factor on microbial denitrification processes, consequently reducing N₂O-N emissions (Ameloot et al., 2013). In addition, the abiotic pathways of N₂O production could be a vital part of the N₂O dynamics in Antarctica soils (e.g. Law and Ling, 2001; Samarkin et al., 2010). Further research is needed to investigate the potential mechanisms for N₂O-N dynamics, especially with field measurements.

5. Conclusions

1. Soils located at greater distance from the glacier front have greater soil development, being more acidic and with greater nutrient contents. They also have more abundant total soil organic C, total N, labile C, recalcitrant C and microbial biomass C. These areas showed the highest CO₂-C emissions and production potentials of CO₂-C and N₂O-N.
2. The humification degree of soil organic matter increases with soil depth and proximity with the glacier front. Hence, the relative proportion of humified organic matter decreased at vegetated sites. Most of these “humified” compounds are of low complexity and are rapidly biodegradable in polar environments.
3. The establishment of cryptogamic vegetation is a key factor for increasing soil organic matter and CO₂-C emissions in recently exposed soils due to glacier recession. Further research is needed to investigate the C balance of these areas.

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