

**UNIVERSIDADE FEDERAL DO PAMPA**  
**CAMPUS SÃO GABRIEL**  
**PROGRAMA DE PÓS-GRADUAÇÃO *STRICTO SENSU* EM CIÊNCIAS**  
**BIOLÓGICAS**

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**FLUXOS DE METANO E ÓXIDO NITROSO EM SOLOS SOB COBERTURAS  
VEGETAIS E INFLUÊNCIA DE AVES EM ÁREA DE DEGELO EM RIP POINT,  
ILHA NELSON, ANTÁRTICA**

**SÃO GABRIEL, RIO GRANDE DO SUL, BRASIL.**

**2012**

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Dissertação apresentada ao programa de Pós-Graduação *Stricto Sensu* em Ciências Biológicas da Universidade Federal do Pampa, como requisito parcial para obtenção do Título de Mestre em Ciências Biológicas.

Orientador: Prof. Dr. Frederico Costa Beber Vieira

**São Gabriel**

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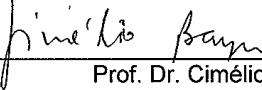
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Área de concentração: Qualidade Ambiental

Dissertação defendida e aprovada em: 12 de dezembro de 2012.

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Dedico este trabalho ao meu amado avô Willie Hubert (*in memoriam*). Força, fé e persistência que me inspiram. Um exemplo a ser seguido.

## **AGRADECIMENTOS**

À Universidade Federal do Pampa, por minha completa formação profissional.

A CAPES, pela concessão da bolsa.

Ao professor Frederico Costa Beber Vieira, pela orientação, apoio e confiança depositada, meu muito obrigado.

Ao professor Dr. Antônio Batista Pereira, pela oportunidade de participar do Projeto Comunidades Vegetais de Área de degelo da Antártica, vinculado ao Módulo 2 do Instituto Nacional de Ciência e Tecnologia – Antártico Pesquisas Ambientais.

À Marinha do Brasil, ao Ministério do Meio Ambiente e ao CNPq, pelo apoio dado durante a XXX Operação Antártica Brasileira (OPERANTAR).

Aos meus colegas e amigos do grupo de solos, pelo apoio dado nas análises das amostras, pelas discussões e trabalhos compartilhados que enriqueceram nosso conhecimento e pelos bons momentos de convívio que serão sempre lembrados com carinho. Em especial à Stefânia Guedes de Godói, pelo apoio, amizade e confiança durante todo o mestrado, e para toda vida.

Aos companheiros de acampamento na Ilha Nelson, pela força e encorajamento a cada momento, pela ajuda nas coletas e pelas horas de convivência que foram de especial importância.

Aos colegas do PPG Ciências Biológicas, e aos queridos Ana Paula Zemolin, Daiana Bortoluzi Baldoni, Danilo Rodrigues de Rodrigues, Renata Figueira Machado e Roberta Aparecida Fantinel, pelo apoio e cumplicidade durante todos os momentos.

À banca examinadora pela disponibilidade e contribuições.

Agradeço em especial à minha família, meus amados pais Eduardo Neufeld e Elvine Hubert Neufeld, e meus irmãos Luciano Hubert Neufeld e Wágner Hubert Neufeld pelo carinho incondicional, apoio e compreensão nesta etapa tão importante. Sem o incentivo de vocês não teria chegado até aqui, muito obrigada por tudo.

A Deus minha eterna gratidão, por colocar em meu caminho cada um mencionado acima, e pela alegria de despertar a cada dia novas curiosidades, dar novos ensinamentos e mostrar que sempre temos mais a aprender e evoluir.

"O que vale na vida não é o ponto de partida  
e sim a caminhada. Caminhando e  
semeando, no fim terás o que colher."

Cora Coralina

## RESUMO

Atualmente é crescente a preocupação com a emissão de gases do efeito estufa (GEE) relacionada ao solo, sendo que dependendo do manejo adotado este pode ser fonte ou dreno de dióxido de carbono ( $\text{CO}_2$ ), óxido nitroso ( $\text{N}_2\text{O}$ ) e metano ( $\text{CH}_4$ ). Porém, sobre o comportamento destes gases em solos de ecossistemas naturais, como as áreas de degelo na Antártica Marítima, pouco se conhece. O presente trabalho objetivou avaliar os fluxos de GEE em solos sob degelo em Rip Point na Ilha Nelson, Antártica e verificar os aspectos no solo e clima que influenciam a emissão e absorção destes gases. Para tanto foram escolhidos cinco locais visando as diferentes coberturas vegetais e presença ou não de aves marinhas. A primeira foi de solo descoberto, a segunda com 100% de cobertura pelo musgo *Sanionia uncinata* e a terceira uma área coberta por líquens. As quarta e quinta áreas sofreram influencia direta da atividade de aves, sendo que uma era coberta pela alga *Prasiola crispa* e outra com a gramínea *Deschampsia antarctica*. A coleta dos gases se deu no período de seis dias no mês de fevereiro de 2012, pelo método de câmaras fechadas, foi coletado de solo para análises químicas e físicas, e monitorada a temperatura do solo e ar, teores de N mineral e umidade do solo. Para o período avaliado as taxas de fluxos de  $\text{N}_2\text{O}$  variaram com média mais alta de  $21,25 \pm 22,14 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$  para área de *P. crispa*, e mais baixa de  $0,11 \pm 1,93 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$ , na área de líquens. Para o  $\text{CH}_4$  somente a área de *P. crispa* apresentou, na taxa média, valores positivos de emissão, com  $0,47 \pm 3,61 \mu\text{g CH}_4 \text{m}^{-2}\text{h}^{-1}$ , sendo que a área de solo descoberto apresentou maior influxo, de  $-11,92 \pm 5,7 \mu\text{g CH}_4 \text{m}^{-2}\text{h}^{-1}$ . Não foi observada correlação entre os fluxos de  $\text{N}_2\text{O}$  e os atributos do solo. O fluxo acumulado de  $\text{CH}_4$  teve correlação com os estoques de Carbono ( $P < 0,01$ ) e Nitrogênio Total ( $P < 0,01$ ) do solo na camada de 0-10 cm. As áreas de solo descoberto e de *S. uncinata* tiveram emissão acumulada de  $\text{N}_2\text{O}$  próximo à Zero, sendo que foram observados eventos de coleta com influxo do gás, podendo ter ocorrido redução do  $\text{N}_2\text{O}$ . A área de solo descoberto teve o maior influxo acumulado de  $\text{CH}_4$  e a área de *P. crispa* foi a única a apresentar emissão acumulada para o período, observando-se que as taxas de fluxos do  $\text{CH}_4$  apresentaram relação direta e significativa ( $P < 0,001$ ) com os teores de amônio do solo. Assim, a influência da

presença de aves parece ter maior efeito nos fluxos de CH<sub>4</sub> e N<sub>2</sub>O do solo do que o tipo de vegetação presente.

Palavras-chave: Metano, Óxido nitroso, aves marinhas, cobertura vegetal, Antártica marítima.

## ABSTRACT

Due to the problem of global warming is growing concern over the soil emission of greenhouse gases (GHG). It is known that the land use for agriculture and livestock, if managed incorrectly, cause severe impacts on the fluxes of carbon dioxide ( $\text{CO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ). But little is known about the behavior of these gases in soils of natural ecosystems. Analyzes of GHG emission or absorption in soil and edaphoclimatic factors that govern these fluxes are scarce in polar environments, such as defrost areas of maritime Antarctic. This study aimed to evaluate the GHG fluxes in soils in thaw areas in Rip Point, Nelson Island, Antarctica and check the soil and climate aspects that influence the emission and absorption of these gases. For both were selected five sites targeting the different vegetation cover and presence of sea birds. The first area was of bare ground, the second with 100% coverage by moss (*Sanionia uncinata*) and the third covered by lichens. The fourth and fifth areas suffered directly influences of the bird's activity, one of which was covered by *Prasiola crispa* algae and other with *Deschampsia Antarctica* grass. The gases sampling occurred in the period of six days in February 2012, by the method of static chambers, and soil sampling was carried for chemical and physical analysis. For the evaluated period  $\text{N}_2\text{O}$  fluxes varied with highest average  $21.25 \pm 22.14 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$  for *P. crispa*, and lowest at  $0.11 \pm 1.93 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$ , in the Lichen soil. For  $\text{CH}_4$  only the area of *P. crispa* showed positive average, with  $0.47 \pm 3.61 \mu\text{g CH}_4 \text{m}^{-2}\text{h}^{-1}$ , and the area of bare soil showed greater influx of  $-11.92 \pm 5.7 \mu\text{g CH}_4 \text{m}^{-2}\text{h}^{-1}$ . No correlation was observed between  $\text{N}_2\text{O}$  fluxes and soil attributes. The accumulated  $\text{CH}_4$  flux correlated with stocks of Total Carbon (<0.01) and Total Nitrogen (<0.01) in the soil layer at 0.00-0.10 m. Areas of bare soil and *S. uncinata* showed accumulated  $\text{N}_2\text{O}$  emission close to zero, and in some collection events were observed gas influx, which may have occurred  $\text{N}_2\text{O}$  reduction. The area of bare soil had the highest cumulative  $\text{CH}_4$  influx and the area of *P. crispa* was the only to be presented cumulative emissions to the period, noting that the  $\text{CH}_4$  showed direct and significant relation with ( $p < 0.001$ ) whit the ammonium ( $\text{NH}_4^+$ ) contents in the soil.

Keywords: Methane, Nitrous Oxide, sea birds, vegetation cover, maritime Antarctica.

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## 1. INTRODUÇÃO

### 1.1. Aquecimento global e seus efeitos

É crescente a preocupação com a problemática das mudanças climáticas nas últimas décadas, e tem-se falado cada vez mais sobre o Efeito Estufa e suas causas. O Efeito Estufa ocorre de forma natural devido à concentração dos gases de efeito estufa (GEE) na atmosfera, e é vital para manter a temperatura do planeta estável. Porém atualmente observa-se um acréscimo nas concentrações desses gases, principalmente Dióxido de Carbono (CO<sub>2</sub>), Metano (CH<sub>4</sub>) e Óxido Nitroso (N<sub>2</sub>O), causado pela atividade humana e tem resultado em um aumento na temperatura do planeta, e por consequência, vem sendo alvo frequente de pesquisadores (Carvalho et al. 2010; Lal, 2004). Estima-se que a alteração na concentração dos GEE desencadeie um aumento na temperatura global em até 0,2°C por década no decorrer do século (IPCC, 2007).

O aumento na temperatura global em sua escala atual e seus efeitos é percebido em todo o planeta, inclusive nas regiões polares. Segundo o IPCC (2007), estas regiões sofrerão grandes impactos com as mudanças climáticas, dentre os quais de destacam a redução em espessura e extensão dos glaciares e mantos de gelo; alterações nos ecossistemas naturais com efeitos prejudiciais para numerosos organismos, em particular para aves migratórias, mamíferos e predadores superiores e comunidades humanas que ali habitam. Existem evidências de que estas mudanças já vêm sido percebidas na Antártica marítima nas últimas décadas, refletidas pela retração das geleiras, aumento médio da temperatura nas ilhas Antárticas, e mudanças em habitats de plantas vasculares e animais (Cook et al. 2005; Smith, 1994; Quayle et al. 2002; Ugolini & Bockheim, 2008; Vaughan et al. 2001). Este quadro pode ser minimizado com práticas que visem mitigar as emissões de gases influentes no aquecimento global, o que ressalta a importância de estudos acerca dos fluxos de GEE.

Dependendo do tipo de uso e das práticas de manejo utilizados, o solo pode ser uma fonte ou um dreno de GEE, e trabalhos investigando essa relação vêm sendo amplamente realizados em sistemas agrícolas (Bayer et al. 2000; Mosier, 1998). Porém, estudos em ecossistemas naturais de regiões austrais, como as

áreas de degelo da Antártica Marítima, acerca dos fluxos de GEE do solo e dos fatores climáticos e edáficos que os governam ainda são muito escassos (Sun et al. 2002; Zhu et al. 2005). O presente trabalho visou contribuir para suprir um pouco esta lacuna.

## **1.2. Rip Point, Ilha Nelson, Antártica**

A Ilha Nelson (lat. 62°14'41" – 62°22'11"S, long. 58°49'30" – 59°15'00"W) é uma das maiores ilhas do Arquipélago de South Shetland e está localizada a sudoeste da Ilha Rei Jorge, perto da parte norte da Península Antártica. Rip Point (lat. 62°14'14" – 62°15'45"S, long. 58°59'13" – 59°02'30"W), nosso local de estudo, está localizado ao norte da Ilha Nelson. Apresentando cerca de 3 km de comprimento e 1,5 km de largura, Rip Point é uma das maiores áreas de degelo na Ilha Nelson (Putzke et al. 1998).

Em Rip Point percebe-se presença de pequenas colônias de aves, principalmente perto da costa litorânea. Em relação à flora local têm-se registros de algas, líquens, gramíneas e várias espécies de musgos (Putzke et al. 1998).

## **1.3. Caracterização dos solos na Antártica Marítima**

Em geral os solos no continente Antártico são descritos como pouco desenvolvidos e pobres em relação aos nutrientes, o que aliado às condições climáticas, agrava as condições para sobrevivência de plantas e habitats para organismos (Bölter, 2011). Porém, na zona costeira da Antártica com áreas de degelo, apresenta formação de Criossolos Ornitogênicos, originados a partir do acúmulo de excrementos de aves. Estes por sua vez são ricos em material orgânico de fácil decomposição, associado a uma matriz rica em minerais como fosfatos e seixos sobre um manto rochoso (Bölter, 2011; Michel et al. 2006).

Em geral solos ornitogênicos apresentam de 10 a 100 vezes maiores teores C orgânico total, N total e número de microrganismos encontrados do que os não ornitogênicos (Aislabie et al. 2008; Gregorich et al. 2006). As entradas de nitrogênio no solo são relacionadas principalmente à presença de aves que nidificam na costa

da Antártica marítima (Bölter, 2011). A entrada de matéria orgânica nestes solos se dá a partir dessas colônias de aves durante o verão, pela deposição de penas, cascas de ovos e restos orgânicos, como excretas (Aislabie et al. 2008).

Os processos biológicos em solos da Antártica marítima se dão pela cobertura vegetal e pela atividade de microrganismos presentes, como bactérias, fungos, microalgas e cianobactérias, além de pequenos nematóides. A disponibilização de nutrientes inorgânicos no solo por processos químicos de intemperismo é lenta, pois este é restrinido pela baixa disponibilidade de água e baixas temperaturas (Bölter, 2011; Michel, 2005). Em áreas de degelo com cobertura vegetal a temperatura do solo pode alcançar mais de 5°C, pela formação de micro-climas locais, favorecendo a colonização por microrganismos e formação de horizonte superficial no solo (Michel, 2005).

#### **1.4. Os fluxos de CH<sub>4</sub> e N<sub>2</sub>O relacionados ao solo e a Antártica marítima**

Em solos de clima subtropical e tropical os fatores abióticos que normalmente regem os fluxos de GEE são a textura, temperatura, umidade do solo, além dos teores de Carbono orgânico total, Carbono lável, Nitrogênio total e Nitrogênio mineral; já dentre os fatores bióticos a atividade microbiana é a principal responsável (Giacomini et al. 2006). A atividade microbiana e as interações entre esta e os fatores pedológicos governam os fluxos de GEE no solo. Uma diminuição da diversidade biológica pode causar uma parcial ou mesmo total perda de importantes processos biológicos do solo, o que acarreta diretamente na emissão desses gases, e tais distúrbios da interação entre parâmetros abióticos e bióticos são apenas parcialmente reversíveis (Borken & Brumme, 1997).

O CH<sub>4</sub> é um importante gás do efeito estufa, e o solo influencia diretamente a emissão ou absorção deste gás. Dois tipos de microrganismos são responsáveis pelas modulações no fluxo terrestre do CH<sub>4</sub>, as bactérias metanogênicas encontradas em geral nos ambientes anaeróbicos, e as metanotróficas em ambientes aeróbicos (Boeckx et al. 1997). No solo estas bactérias conseguem coexistir em micro-habitats e, juntas, regulam os fluxos de CH<sub>4</sub> para os ecossistemas (Price et al. 2004).

Para climas tropicais e temperados a absorção de CH<sub>4</sub> atmosférico no solo é em grande parte controlada pela porosidade e umidade deste, sendo que as taxas de absorção de CH<sub>4</sub> em geral aumentam com a diminuição da umidade. Poros saturados por água, ambiente anóxico, altas temperaturas no solo, potenciais redox em valores negativos, decomposição de material orgânico e atividade de comunidades metanogênicas levam a uma emissão líquida de CH<sub>4</sub> (Borken et al. 2005; Dalal et al. 2008; Tate et al. 2007). A textura do solo influencia indiretamente na emissão de CH<sub>4</sub>. Solos de textura mais arenosa, devido a sua maior macroporosidade apresentam melhor efeito na difusão do CH<sub>4</sub> do que solos argilosos, e, portanto se percebe mais oxidação de CH<sub>4</sub> (Boeckx et al. 1997).

Em áreas de degelo da Antártica marítima tem se observado que em solos ornitogênicos a emissão de CH<sub>4</sub> é em média, significativamente maior do que os solos não ornitogênicos, o que é relacionado ao alto teor de C na matéria orgânica destes solos (Sun et al. 2002; Zhu et al. 2008a). A posição na paisagem e as características de drenagem do solo, além da temperatura de ar e solo, afetam a emissão de CH<sub>4</sub>, sendo que, como em áreas de clima tropical, solos melhor drenados mostraram maior capacidade de influxo de CH<sub>4</sub>, mas mesmo solos mal drenados na Antártica podem apresentar influxo líquido de CH<sub>4</sub> (Vieira et al. 2012).

O solo é a principal fonte de N<sub>2</sub>O para a atmosfera, sendo produzido em duas transformações do N no solo (Bremner, 1997). A nitrificação é a primeira delas e ocorre naturalmente em solos bem drenados, onde o NH<sub>4</sub><sup>+</sup> é preferencialmente transformado em nitrato (NO<sub>3</sub><sup>-</sup>) (Takaya et al. 2003). O processo ocorre em duas etapas mediadas por bactérias autotróficas. Fatores no solo que favorecem a nitrificação são: pH elevado, suprimento de O<sub>2</sub>, temperatura, umidade e teor de NH<sub>4</sub><sup>+</sup> presente (Bissani et al. 2008). A segunda transformação, que para o presente trabalho é a mais crítica por liberar maiores quantidades de N<sub>2</sub>O para a atmosfera, é a desnitrificação. Esta se dá em condições anaeróbias, onde o NO<sub>3</sub><sup>-</sup> funciona como acceptor final de elétrons, sendo reduzido à N<sub>2</sub> (Takaya et al. 2003). O O<sub>2</sub> é considerado fator limitante para a desnitrificação, e as condições no solo que propiciam a falta de O<sub>2</sub> são alagamentos, intensa atividade biológica e grande quantidade de matéria orgânica decomponível (Bissani et al. 2008). A umidade e a

temperatura do solo são fatores que afetam diretamente os processos de nitrificação e desnitrificação (Giacomini et al. 2006), refletindo assim nos fluxos de N<sub>2</sub>O no solo.

O N<sub>2</sub>O em solos da Antártica marítima tem apresentado relação com a temperatura do solo, com a profundidade do lençol freático e principalmente com a abundância de N no solo, oriundo dos dejetos de aves marinhas (Zhu et al. 2008b). A precipitação também influí sobre os fluxos de N<sub>2</sub>O, sendo que análises em solos ornitogênicos e não ornitogênicos durante a transição entre épocas chuvosas e mais secas de verão mostram mudanças nas emissões de N<sub>2</sub>O (Sun et al. 2002).

A recente problemática do Aquecimento Global tem cada vez mais enfoque na pesquisa. Sabe-se que o fluxo de GEE relacionado ao solo é influenciado pelas diferentes características bióticas e abióticas do mesmo, e que estas interferem diretamente na emissão e absorção de N<sub>2</sub>O e CH<sub>4</sub> em áreas cultivadas. Porém, pouco se sabe sobre a magnitude do fluxo desses gases, e sobre como os fatores de solo e clima afetam seu comportamento em regiões de ecossistemas naturais, como as áreas de degelo na Antártica marítima.

O continente Antártico têm 98% de sua área coberta permanentemente por gelo e os 2% restantes apresentam-se sob degelo no verão (Campbell and Claridge, 1987). Nesta área livre de gelo, que abrange aproximadamente 280 000 km<sup>2</sup>, se dão a maioria das atividades orgânicas existentes na região. Estudos mostram diferenças nas emissões de CH<sub>4</sub> e N<sub>2</sub>O conforme as características do solo e posição na paisagem em áreas de degelo ao longo da costa, entretanto, os fatores edáficos desta região que governam os fluxos de GEE não são conhecidos, o que torna este tipo de estudo importante para se estimar a contribuição no Potencial de Aquecimento Global (PAG) que estes locais de degelo representam.

## 2. HIPÓTESE GERAL

A cobertura vegetal e a presença e atividade de aves marinhas sobre o solo, em Rip Point na Ilha Nelson, afetam em magnitudes diferentes os fatores que governam os fluxos de CH<sub>4</sub> e N<sub>2</sub>O em solos de áreas de degelo da Antártica marítima.

## **2.1. Hipóteses específicas**

Em solos sob atividade de aves os estoques de Carbono orgânico total e de Nitrogênio total são maiores do que em outros locais devido ao aporte de dejetos pelas aves. Isto faz com que a emissão de CH<sub>4</sub> e N<sub>2</sub>O seja maior nestas áreas que nas demais.

A presença de cobertura vegetal favorece a absorção de CH<sub>4</sub> no solo quando o local é bem drenado, enquanto que em locais mal drenados beneficia o efluxo do gás.

## **3. OBJETIVO GERAL**

Avaliar os fluxos de CH<sub>4</sub> e N<sub>2</sub>O no solo em áreas de degelo em Rip Point na Ilha Nelson em diferentes locais da paisagem, observando formações vegetais e presença e atividade de aves marinhas, e verificar os principais fatores de solo e clima envolvidos na emissão e absorção destes gases.

### **3.1. Objetivos específicos**

Avaliar a relação entre as coberturas vegetais e a presença de aves com os fluxos de CH<sub>4</sub> e N<sub>2</sub>O em solos de áreas de degelo na Antártica.

Monitorar os fatores de clima e fatores químicos e físicos de solo nos locais de degelo e correlacioná-los com os fluxos de Gases do Efeito Estufa locais.

Quantificar os estoques de Carbono orgânico total (COT), Carbono Orgânico Particulado (COP) e Nitrogênio total (NT) no solo em áreas de degelo e correlacioná-los aos fluxos de CH<sub>4</sub> e N<sub>2</sub>O.

Estimar o Potencial de Aquecimento Global (PAG) de áreas de solo sob diferentes coberturas vegetais e atividade de aves marinhas em locais de degelo em Rip Point na Ilha Nelson, Antártica.

#### **4. APRESENTAÇÃO DO MANUSCRITO**

O presente trabalho será apresentado na forma de artigo, com formatação conforme as normas da revista Geoderma. Está dividido em introdução, material e métodos, resultados, discussão e conclusões.

## 5. MANUSCRITO

**Title: Methane and nitrous oxide fluxes under vegetation covers and bird activity in ice-free soils of Rip Point, Nelson Island, South Shetland, Antarctica**

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## Abstract

Little is known about greenhouse gases (GHG) in tundra soils covered with mosses or lichens, distributed in areas free of permanent snow cover during part of the summer in the Antarctic Peninsula. The aim of this study was to quantify the nitrous oxide ( $N_2O$ ) and methane ( $CH_4$ ) fluxes in sites under different vegetation covers and with or without bird activity, using the static chamber method, on Rip Point, Nelson Island, in the Maritime Antarctic. Soil mineral nitrogen contents, temperature and water-filled pore space were monitored, and the content of total organic carbon (TOC), particulate organic carbon (POC), total nitrogen (TN), bulk density and texture were determined aiming to identify controlling variables of  $N_2O$  and  $CH_4$  emissions. The evaluated sites were soils covered by: a) moss carpet of *Sanionia uncinata*; b) lichens; c) *Prasiola crispa* algae; d) *Deschampsia antarctica* grass; and e) bare soil. The soils covered by algae and grass had influences of giant petrels (*Macronectes giganteus*) nesting fields. Flux rates of both  $N_2O$  and  $CH_4$  were relatively low for all sampling events. Mean  $N_2O$  flux rates ranged from  $0.11\pm1.93$  up to  $21.25\pm22.14 \mu g N_2O m^{-2} h^{-1}$  for the soils under *P. crispa* and Lichen soil, respectively. For the  $CH_4$  fluxes only the area of *P. crispa* showed positive mean, with  $0.47\pm3.61 \mu g CH_4 m^{-2} h^{-1}$ , while the greatest absorption rate was observed in the bare soil, with influx of  $-11.92\pm5.7 \mu g CH_4 m^{-2} h^{-1}$ . Areas of bare soil and *S. uncinata* had their  $N_2O$  accumulated emissions close to Zero, and these two sites had  $N_2O$  influx rates in two sampling events, probably favored by conditions of low temperature, high soil moisture and low mineral N content in soil, but no significant relation ( $P>0.05$ ) was observed for the fluxes and these variables. Net accumulated  $CH_4$  emission was observed only in the area of *P. crispa*, where the giant petrels activity was accentuated, and close relation was found between  $CH_4$  fluxes and  $NH_4^+$ , ( $P<0.001$ ), while the area of bare soil acted as an important sink of  $CH_4$ , probably favored by the coarse texture of the site. The moss carpet with negligible ornithogenic influence had the largest C and N stocks ( $P<0.05$ ).

**Keywords:** Methane, nitrous oxide, seal birds, vegetal cover, Maritime Antarctica

## Introduction

Climate change has been a major issue in recent decades, in which the greenhouse effect and its causes are nowadays a crucial question in the worldwide research. The concentration of greenhouse gases (GHGs), mainly carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ), is increasing fastly in the atmosphere. It is estimated that the change in the GHG concentration in atmosphere will imply an increase in global temperature in up to 0.2 °C by decade during the course of the century (IPCC, 2007). There are evidences that this warming has arised dramatically over the last half century in the maritime Antarctica, especially along the western Antarctica Peninsula (Vaughan et al. 2001).

The GHG fluxes in soils have been widely studied in agricultural regions because, depending on type of use and management practices employed, the soil can be a source or a sink of GHG (Mosier, 1998). However, the magnitude of these GHG fluxes and their main soil and climatic factors that influence natural austral ecosystems in areas of melting, as the maritime Antarctica, came to be evaluated only from the last decade, and these studies are still scarce (Sun et al. 2002; Vieira et al. 2012; Zhu and Sun, 2005; Zhu et al. 2005).

The tundra soils covered with mosses or lichens of the Antarctic Peninsula are distributed in areas free of permanent cover snow during part of the summer and comprise about 8% of the maritime Antarctica (Sun et al. 2002; Zhu et al. 2005). They comprehend large areas of vegetation with mosses and lichens, and occasionally there is the presence of species of higher plants (Putzke et al. 1998). These soils, called Cryosols, are the result of cycles of freezing and thawing, of biogeochemical processes under each vegetation type, and also of its colonization by penguins and other seabirds and subsequent deposition of their

droppings, which strongly affect the attributes of these soils (Sun et al. 2002, Ugolini and Bockheim, 2008).

Ornithogenic Cryosols in general occur at active or abandoned penguin rookeries (Simas et al. 2008) and are particularly fertile, imparted by the large deposition of sea animal excreta, and have high levels of organic carbon (CO), nitrogen (N) and phosphorus (Sun et al. 2002; Zhu et al. 2008c). They usually have a great content of easily degradable C in its organic matter and may be vulnerable to losses to the atmosphere in response to the increasing of the temperature (Michel et al. 2006). A large contribution of mineral N forms to the total N can be found in these soils, mainly as ammonium ( $\text{NH}_4^+$ ) but also eventually as high levels of nitrate ( $\text{NO}_3^-$ ) (Aislabie et al. 2008; Gregorich et al. 2006), enhancing the potential for  $\text{N}_2\text{O}$  emission (Zhu et al. 2008c).

Tundra soils with intense bird activity, by penguins or seabirds have been pointed out by several authors as sources of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  into the atmosphere, if compared to soils without the presence of birds (Gregorich et al. 2006; Sun et al. 2002; Zhu and Sun, 2005; Zhu et al. 2008b; Zhu et al. 2009). Relatively high  $\text{CH}_4$  and  $\text{N}_2\text{O}$  emission rates have been reported in these ecosystems (Sun et al. 2002; Zhu et al. 2005; Zhu et al. 2008a).

In tropical and subtropical soils, the main factors that govern the fluxes of GHGs are the C and N contents and the biological activity, as well as texture, temperature and humidity (Boeckx et al. 1997, Giacomini et al. 2006, Gomes et al. 2009, Mosier et al. 1991). However, in Cryosols of the maritime Antarctica less is known about the way and the effectiveness in which these factors affect such fluxes. Studies on the fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  demonstrated that the emission has been correlated to higher temperatures in the soil surface layer, and the precipitation and amount of N in the soil, respectively (Gregorich et al. 2006; Sun et al. 2002, Zhu et al. 2007). These soil ecosystems seem to be particularly sensitive to climate change,

and understanding the biogeochemical processes occurring in them is essential for predicting their responses to these changes (Shaver et al. 2000; Park et al. 2007).

This study aimed to evaluate the GHG fluxes in thawing soils under different vegetation covers and with or without bird activity in Rip Point on Nelson Island, Antarctica, and check the soil and climate aspects of the region that influence the emission or mitigation of these gases.

## 1. Materials and methods

For this study, samples were collected in February 2012, during the 30<sup>th</sup> Brazilian Antarctic Operation, and the GHG fluxes were evaluated in north of Nelson Island, in Rip Point (lat. 62°14'14" – 62°15'45"S, long. 58°59'13" – 59°02'30"W), Antarctica (Fig.1).

Insert Fig.1.

Five sites were selected in the area, in order to get different characteristics of soil, vegetation cover and bird activity. The first site was a bare soil, with evidence of alluvial formation. The second, an area with 100% coverage by a moss carpet of *Sanionia uncinata* (Hedw) Loesk, with the water table near the surface, ranging from approximately 20-30 cm in depth and characterizing a poorly drained soil. The third area was mostly covered by lichen species, showing a great local diversity. In this area, individuals of *Ochrolechia frigida* (Sw.) Lynge, *Usnea antarctica* Du Rietz, *Polytrichum juniperinum* Hedw, *S. uncinata*, *Prasiola crispa* (Lightfoot) Menegh., *Sphaerophorus globosus* (Huds.) Vain, *Schistidium urnulaceum* and *Psoroma cinamomeon* Malme were found. The site was about 30 m distant from a nesting area of giant petrels (*Macronectes giganteus*, Gmelin, 1789) and, although the natural drainage was not directly linked to the sampling area, the vegetation and soil characteristics indicate that the area has been weakly influenced by this community. The fourth and fifth

sites were located near the nesting areas of giant petrels. The first one was mainly covered by the alga *P. crispa*, but some individuals of the lichen *P. juniperinum* were also registered. In the second, vegetation was largely dominated by *D. antarctica* grass, with points of *Syntrichia magellanica* (Mont) R.H. Zander H, *P. crispa* and *S. uncinata*. The soil of the fourth and fifth sites is evaluated as ornithogenic Cryosol, considering that in places of Admiralty Bay they had means of  $32.0 \pm 29.0 \text{ g kg}^{-1}$  of TOC and  $4.3 \pm 1.0 \text{ g kg}^{-1}$  NT at the layers 0-0.60 m (Simas et al. 2008).

The sites are herein called according to their predominant vegetation cover, as follows: Bare soil, *S. uncinata*, lichen soil, *P. crispa* and *D. antarctica*.

### 1.1. Sampling and analysis of GHG emissions

Four sampling events of GHG were taken in the areas Bare soil, *S. uncinata*, Lichen soil and *P. crispa* at 10.02.2012, 12.02.2012, 14.02.2012 and 16.02.2012. Sampling in the area of *D. antarctica* were performed only for two last sampling data, due to logistical difficulties. Severe weather conditions and an early decamping led to a reduced sampling period. Gas sampling was carried out through static PVC chambers of 10 cm height and 25 cm diameter. Each chamber was supported by a metal base fixed on the ground, with a cannula with water, to isolate the inside from the outside and prevent gases exchange. Three cameras were randomly installed in each collection area, in order to obtain three replications.

Samples were obtained by polypropylene syringes with triple Luer Lock valve, during the morning (starting at about 9 a.m. and sampling at time intervals of 0, 30, 60 and 90 minutes after closing the chambers). Air samples were immediately injected into glass vials Exetainer® 12 ml (Labco Ltd, High Wycombe, United Kingdom), and the concentrations of CH<sub>4</sub> and N<sub>2</sub>O in the samples were determined by gas chromatography (Shimadzu GC2014

“Greenhouse” model), at the lab of Environmental Biogeochemistry (UFRGS), soon after the return from Antarctica. The chromatograph was equipped with three columns and work at temperature of 70 °C, the carrier gas was N<sub>2</sub>, at a flow of 26 mL min<sup>-1</sup>, injector with direct sampling grid of 1 mL with temperature at 250 °C, electron capture detector (ECD) to 325 °C for detecting N<sub>2</sub>O and flame ionization detector (FID) at 250 °C for CO<sub>2</sub> and CH<sub>4</sub>. To estimate the gas fluxes were used the equation below:

$$f = \frac{\Delta Q}{\Delta t} \frac{PV}{RT} \frac{1}{A}, \quad (\text{Equation 1})$$

where  $f$  is the gas flux ( $\mu\text{g m}^{-2} \text{ h}^{-1}$  N<sub>2</sub>O or CH<sub>4</sub>), Q is the quantity of gas ( $\mu\text{g N}_2\text{O}$  or CH<sub>4</sub>) in the chamber, P is the atmospheric pressure (atm) in the inner chamber, V is the chamber volume (L), R is the constant for ideal gases (0.08205 atm.L mol<sup>-1</sup>K<sup>-1</sup>), T is the chamber temperature (K) and A is the base area of the chamber (m<sup>2</sup>). Rates of increase in gas concentration inside the chamber were estimated by the angular coefficient from the linear regression adjusted from the relation between time and gas concentrations (Gomes et al. 2009; Vieira et al. 2012).

The accumulated emission of gases (CH<sub>4</sub> and N<sub>2</sub>O) for the six day period was estimated from the integration of the area below curves in the relation between daily flux rates and sampling time. Because the sampling period in the area of *D. antarctica* was shorter, we estimated the value of the area for three days and extrapolated for the total period of evaluation. In order to estimate the relative contribution of each gas, the partial Global Warming Potential (pGWP) was calculated by taking into account only net balance of N<sub>2</sub>O and CH<sub>4</sub> fluxes, in equivalent-carbon.

Simultaneously to the air sampling, the soil temperature and the temperature inside in the chamber were monitored. In each event, soil samples of 0-0.05m layer were taken in triplicate for soil gravimetric moisture (oven-dried at 105 °C up to constant weight) and mineral nitrogen content ( $\text{NO}_3^-$  and  $\text{NH}_4^+$  by extraction with 1M KCl and semi-micro Kjeldahl distillation).

### 1.2. Soil sampling and analysis of chemical and physical attributes

Soil samples were collected in three replicates per area, at the layers 0-0.05, 0.05-0.10, 0.10-0.20 and 0.20-0.40 m, packed in plastic flasks and analyzed immediately after returning from Antarctica. The samples were dried in an oven at 50 °C, ground in a hammer mill and sieved (2 mm). Total Nitrogen (TN) contents were determined by wet digestion and semi-micro Kjeldahl distillation. Labile carbon contents were obtained by the particle size physical fractionation of organic matter (Vieira et al. 2007), in which the C content in the particulate organic carbon (POC) was determined by dry combustion using a Shimadzu TOC analyzer (CO-VCSH®, Shimadzu Corp., Kyoto, Japan). Soil sub-samples were subjected to grinding in a porcelain mortar (<0.05 mm) for analysis of total organic carbon (TOC) content by dry combustion using the same TOC analyzer described above.

Soil bulk density was determined by the core method (Blake and Hartge, 1986), and the estimation of water-filled pore space (WFPS) was performed from the values of soil bulk density and assuming a particle density of  $2.65 \text{ g cm}^{-3}$  (Gomes et al. 2009). Clay, silt and sand contents were determined by the pipette method according to Tedesco et al. (1995) (Table 1).

Insert Tab. 1.

### 1.3. Statistical Analysis

The relationship between flux rates of GHG and climate and soil variables was performed by Pearson correlation. The accumulated GHGs emissions and the TOC, POC and NT contents at the different sites were subjected to one-way ANOVA. Different means were separated by the Tukey test ( $P<0.05$ ).

## 2. Results

The highest  $\text{N}_2\text{O}$  emission rates throughout the period were observed from the soils with *P. crispa* and *D. Antarctica*, which are the sites with presence of birds near to the sampling areas. The largest emission peak occurred on the second day in *P. crispa*, with  $53.83 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$  (Fig. 2a), coinciding with a saturation of soil pores with water and with large mineral N contents ( $\text{NH}_4$  and  $\text{NO}_3$ ) in the soil (Fig. 3a, b, d). However, considering all sites and sampling dates, no significant relation was found between the emission of this gas and soil variables (Table 2). In the second emission peak in the area, with  $15.45 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ , the soil was drained, with 67% of its pores saturated by water. In areas with supposedly negligible influence of birds the emissions were lower, kept below  $5.0 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ , except on the first sampling day in the lichen soil, which peaked at  $18.11 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ . The bare soil had influx rates of  $\text{N}_2\text{O}$  during part of the period, as well as the soils under *S. uncinata* and lichens on the third collection event.

Insert Fig. 2.

Insert Fig. 3.

Insert Tab. 2.

The influx of  $\text{CH}_4$  prevailed in most of the evaluation period, and the average daily fluxes ranged from  $-16.99 \pm 13.57$  to  $4.11 \pm 4.54 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$  among the five sites herein

evaluated (Fig.2b). On the first day of sampling the CH<sub>4</sub> emission occurred at three places, with values of 4.02 and 3.5 µg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> in the areas of *S. uncinata* and *P. crispa*, respectively. Only in the site of *P. crispa* we observed CH<sub>4</sub> emission again, on the third sampling day, with 4.11 µg CH<sub>4</sub> m<sup>-2</sup>h<sup>-1</sup> (Fig. 2b). For the rest of the period the soil acted as a sink of CH<sub>4</sub>, and the bare soil had the largest oxidation rates over the most period, except on the last day of sampling, where the lichen soil showed the greatest oxidation rate. The NH<sub>4</sub><sup>+</sup> in soil showed direct relationship ( $P < 0.001$ ) with the CH<sub>4</sub> fluxes rates (Table 2).

The accumulated emission of CH<sub>4</sub> for the six days of sampling showed that the soil with *P. crispa* was the only one to present net emission of this gas in net balance, with production of about 0.60 g C-CH<sub>4</sub> ha<sup>-1</sup> (Fig. 4a). The other sites behaved as CH<sub>4</sub> sinks during the period, with the largest accumulated CH<sub>4</sub> uptake in the bare soil, which oxidized approximately 12 g C-CH<sub>4</sub> ha<sup>-1</sup>. Regarding the N<sub>2</sub>O, all the sites had net accumulated emissions for the six day-period. The largest occurred from the soils of *P. crispa* and *D. antarctica*, with 21.94 and 13.88 g N<sub>2</sub>O-N ha<sup>-1</sup>, respectively. There was no significant difference for the accumulated emissions among the other sites (Fig. 4b). The cumulative N<sub>2</sub>O flux showed no significant correlation with soil attributes, but they were slightly related ( $P < 0.10$ ) to the TOC and TN stocks in the 0-0.05 cm layer. In terms of accumulated emissions of the two gases in C equivalent to six days, it is clear that in the net balance the N<sub>2</sub>O was predominant (Fig. 4c).

Insert Fig. 4.

The soil with *S. uncinata* had predominantly larger contents of TOC, POC and TN than the other areas, and the largest amount of TOC and POC on the site was observed in the 5-10 cm layer, with a content of 40.80 and 21.80 g C dm<sup>-3</sup>, respectively, as well as TN with 6.05 g N dm<sup>-3</sup> (fig. 5). However, in the superficial soil layer at 0-5 cm, greater contents of

TOC, POC and TN were observed in the soil under *P. crispa*, with 42.41 and 15.10 g C dm<sup>-3</sup> and 5.43 g N dm<sup>-3</sup>, respectively, with the greatest gradient in the soil profile in comparison to the other sites. The lichen soil showed its larger contents of these attributes in the third layer, at 10-20 cm, with 30.85 and 13.72 g C dm<sup>-3</sup> and 4.30 g N dm<sup>-3</sup>, respectively. The bare soil exhibited similar TN values along the profile, ranging between 0.17 and 0.05 g N dm<sup>-3</sup> (Fig. 5c), however, in relation to the TOC and POC, the content increased with depth (Fig. 5a, b). The soil under *D. antarctica* showed one of the lowest values of TOC and TN content in all layers, only higher than those in bare soil, and the COP was the lowest of all areas evaluated, except in the 0-5 cm layer, where the first had about 5.0 g C dm<sup>-3</sup>, whereas the second had only 1.25 g C dm<sup>-3</sup> (Fig. 5b).

Insert Fig. 5.

The stocks of TOC, POC and TN for the 0-0.10 m soil layer were closely and positively related to the CH<sub>4</sub> accumulated emission, but the same did not occur for the N<sub>2</sub>O accumulated emission (Table 3). The largest stocks of TOC, POC and TN were found in soil under *S. uncinata*, with 129.9, 60.5 and 18.4 Mg ha<sup>-1</sup>, respectively (Fig. 6). Regarding the TOC, the areas of lichen soil and *P. crispa* were significantly equal, and *D. antarctica* did not differ from the bare soil (Fig. 6a). As for the COP, the soil stock under *D. antarctica* had the lowest values among all the analyzed areas (Fig. 6b), while for the NT the smallest stock was found in the bare soil, with less than 0.25 Mg ha<sup>-1</sup> (Fig. 6c).

Insert Tab. 3.

Insert Fig. 6.

### **3. Discussion**

#### **3.1. Effect of the birds activity and vegetation cover in the fluxes of N<sub>2</sub>O and CH<sub>4</sub>**

In this study, we observed relatively low GHG emissions, with N<sub>2</sub>O and CH<sub>4</sub> fluxes with similar or lower magnitude to those already reported in previous studies in the thawing areas of the maritime Antarctica. There was a clear relationship between the activity of seabirds and the N<sub>2</sub>O and CH<sub>4</sub> flux rates in these soils. Such relation has been reported in other studies, showing that the presence of birds in local soils influence the biogeochemical cycles in this environment, being observed higher emissions of N<sub>2</sub>O and CH<sub>4</sub> (Simas et al. 2007; Sun et al. 2002; Zhu et al. 2005). Environmental variables such as soil temperature and moisture did not influence significantly these fluxes in our study, which was also pointed out in Garwood Valley (Gregorich et al. 2006) for N<sub>2</sub>O and in Field Peninsula (Sun et al. 2002) for CH<sub>4</sub>.

In areas with influence of giant petrels, significantly higher N<sub>2</sub>O emission was observed if compared with the other areas. The abundance of N originated from the activity of seabirds contributes as a source to high N<sub>2</sub>O emissions (Sun et al. 2002; Zhu et al. 2008a). The soil with *P. crispata* had the largest N<sub>2</sub>O accumulated emission, and was observed a decline of NH<sub>4</sub><sup>+</sup> and an increased of NO<sub>3</sub><sup>-</sup> during the sampling periods, suggesting nitrification. Sun et al. (2002) suggested that in ornithogenic soils the production of N<sub>2</sub>O shall be given mainly by nitrification of NH<sub>4</sub><sup>+</sup>. The area had the highest emission peak among all evaluated sites, with 53.83 µg N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>, but this value is still considered low when compared to the average emission of N<sub>2</sub>O in studies like that of Zhu et al. (2008c), who obtained approximately 180 µg N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>, in soils under seabirds activity, in Fildes Peninsula.

The daily N<sub>2</sub>O flux evaluated in *D. antarctica* during the analysis period has coincided with a WFPS above 80%, suggesting conditions for denitrification. Similar results were found by Vieira et al. (2012). Among the evaluated areas, this was the one with the highest temperature in the sampling period. Higher temperatures and soil moisture contributes to the

processes of denitrification in the soil, thereby accentuating the loss of N by N<sub>2</sub>O (Sun et al. 2002), but even below freezing temperatures the microbial activity can lead to emission of the gas, and studies reported denitrification activation in soils at -2 °C (Dorland and Beauchamp, 1991; Müller et al. 2002).

Areas of bare soil and *S. uncinata* had their N<sub>2</sub>O accumulated emissions close to Zero, which was also observed in a bare alluvium soil of an adjacent island, in Hennequin Point (Vieira et al. 2012). These two sites had N<sub>2</sub>O influx rates in two sampling events, while the lichen soil had influx in one sampling day. Net N<sub>2</sub>O uptake is not very common in non-polar soils, as this process seem to be favored in conditions of low temperature, high soil moisture and low N content in soil (Sun et al. 2002; Zhu et al. 2005). The high solubility of N<sub>2</sub>O in water could mean that this molecule is a readily available electron acceptor in natural environments, and the reduction of N<sub>2</sub>O occurs when there is production of the enzyme N<sub>2</sub>O reductase of some bacteria in anaerobic conditions (McEwan et al. 1985). This reduction of N<sub>2</sub>O can be consumed by denitrification, and the rate of N<sub>2</sub>O uptake depends on soil properties, such as the availability of mineral N, soil oxygen and water content, soil temperature and the availability of labile organic C and N (Chapuis-Lardy et al. 2007). The areas of *S. uncinata* and lichen soil showed the lowest soil temperatures, and the three mentioned areas had the WFPS above 70% throughout the period of analysis, with low mineral N contents and, therefore, theoretically had appropriate conditions for negative N<sub>2</sub>O fluxes.

The fluxes average of N<sub>2</sub>O was during the evaluation period at 0.84±2.89, 1.13±2.71, 0.11±1.93, 21.25±22.14 and 15.04±8.74 µg N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup> for the Bare soil, *S. uncinata*, Lichen soil, *P. crispa* and *D. antarctica*, respectively. It is observed that the ornithogenic soil presents a gas emission over 10 times greater than the bare soil. The fluxes rate of the gas

varied greatly between the sampling days, being more constant only in bare soil and in *S. uncinata*. The emission values in these ornithogenic soils were low when compared with values found in Fildes Peninsula, where in the soils under seabird colonies been obtained an average of  $189 \pm 204 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$ , and much lower than local with penguins activity, with an average of  $856 \pm 940 \mu\text{g N}_2\text{O m}^{-2}\text{h}^{-1}$  (Zhu et al. 2008c).

The average  $\text{CH}_4$  flux rates in the period were  $-11.92 \pm 5.7$ ,  $-0.23 \pm 3.01$ ,  $-5.35 \pm 4.31$ ,  $0.47 \pm 3.61$  and  $-3.69 \pm 2.02 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$ , for the areas of Bare soil, *S. uncinata*, Lichen soil, *P. crispa* e *D. antarctica*, respectively. The values observed in the soils under influence of petrels were relatively low when compared with those observed by Sun et al. (2002), that documented an average flux rate of  $227.97 \pm 212.9 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$  in ornithogenic soils, and by Zhu et al. (2008b) that reported an average of  $23.97 \pm 7.7 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$ .

The daily flux of  $\text{CH}_4$  showed a gas mitigation most of the evaluation period, and had a low temporal and spatial variation of fluxes during the studied ranged from  $-16.99 \pm 13.57$  to  $4.11 \pm 4.54 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$  among the five sites herein evaluated, different from two lakes of Millor Peninsula, where present a consistent variation, which -6.2 to 233.6 and -15.1 to 165.2  $\mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$ , and these variation corresponding to the water and air temperature (Zhu et al. 2010).

The accumulated  $\text{CH}_4$  emission was observed only in the area of *P. crispa*, where the giant petrels activity was accentuated. In addition, this area had the highest concentration of mineral N, which is attributed to the intense deposition of fresh manure in the soil (Sun et al. 2002). There was a close relation ( $P < 0.001$ ) between the  $\text{CH}_4$  flux rates and the content of mineral N in soil, particularly with  $\text{NH}_4^+$ . This result indicates that, in this soil, the amount of  $\text{NH}_4^+$  probably reached values where inhibition of the enzyme monooxygenase came to be

effective, inhibiting the activity of oxidation of CH<sub>4</sub> (Boeckx et al. 1997; Dalal et al. 2008; Hütsch, 1998; Hütsch, 2001; Regina et al. 2007).

The area of bare soil acted as a sink of CH<sub>4</sub> throughout the sampling period, which was also observed by Vieira et al. (2012) in soils of Hennequin Point, King George Island. Aerated, non-degraded soils may act as CH<sub>4</sub> sink because this gas can be oxidized to CO<sub>2</sub> by the biological activity or incorporated into microbial biomass (Hütsch, 2001). However, the area presented the WFPS around 70% during the study period, which have been cited as a threshold value for aerobic condition, but the methanotrophic activity persisted intense. Khalil and Baggs (2005) have observed that optimal WFPS conditions for the CH<sub>4</sub> oxidation are around 45%, however in their study was also found methanotrophic action in WFPS at 75%. In the present study the oxidation can be attributed to the coarse texture of the place, with very low clay content in the soil profile, which imparts a high macroporosity, where even in high soil moisture the aeration is still sufficient for the activity of aerobic microorganisms.

### 3.2. Effect of the TOC, POC and TN stocks in the accumulated fluxes of CH<sub>4</sub> and N<sub>2</sub>O

Significant correlation was obtained between the stocks of TOC, POC and TN in the 0-0.10 m soil layer and CH<sub>4</sub> accumulated flux. In the areas with largest TN stocks the gas fluxes was closer to zero. The stocks of TOC and TN were greatest in soil under *S. uncinata*. Soils under more developed vegetation, such as areas with continuous coverage of mosses communities, present higher values of TOC and TN (Simas et al. 2007). However, ornithogenic soils have higher CH<sub>4</sub> emissions when compared to the soil without birds influence (Sun et al. 2002). In the present study, this accumulated emission was observed in *P.crispa*, with very low value and not reaching 1.0 C-CH<sub>4</sub> g ha<sup>-1</sup>, and the area of *D. antarctica* behaved like a CH<sub>4</sub> drain in the study period.

The soil with *D. antarctica* showed N<sub>2</sub>O accumulated emission levels higher than the other evaluated areas, as in *P. crispa* area, however relatively low values considering the proximity of the nests of giant petrels on the site. One can relate this lesser emission to the low TOC and POC stocks, with 35.8 and 7.3 Mg ha<sup>-1</sup>, respectively, and TN, 6.3 Mg ha<sup>-1</sup>, which may be attributed to the physical soil characteristics of the site, such as low level of clay and soil slope by high gradient (about 25%).

### 3.3. Relative contribution of N<sub>2</sub>O and CH<sub>4</sub> fluxes to partial Global Warming Potential

The results of the partial Global Warming Potential, estimated in this study, indicated that the N<sub>2</sub>O was responsible for the main contribution between the gases herein evaluated (Fig.4c). The soils with lichen and *P. crispa* showed the greater contributions, followed by the site of *D. antarctica*. The bare soil showed absorption of gases in the net balance, which is in agreement with that observed in Hennequin Point (Vieira et al. 2012). Taking into account that uncovered soils represent a large percentage of area of the thaw soils in the maritime Antarctica, this result indicates that the bare soil is highlighted with a large mitigation potential for greenhouse gases from atmosphere. The benefic effect regarding the CH<sub>4</sub> and N<sub>2</sub>O fluxes in such areas is enhanced by their potential of C sequestration if they experience future colonization and/or vegetal development. Specific studies are required to address the mitigating potential found in these soils.

## 4. Conclusions

1 - The areas with the birds influence, *D. antarctica* and *P. crispa*, showed the highest emissions of N<sub>2</sub>O.

2 – Net absorption of CH<sub>4</sub> predominated in the evaluated areas. The bare soil presented the greatest CH<sub>4</sub> influx and the smallest N<sub>2</sub>O emission, resulting in the largest potential for

mitigating GHG in the maritime Antarctica. The mechanism of the fluxes in areas of bare soils needs further studies.

3 - The daily CH<sub>4</sub> fluxes had close and direct relation with soil NH<sub>4</sub><sup>+</sup> contents, while the accumulated CH<sub>4</sub> flux was closely and directly related with the TOC, POC and TN stocks in the 0-10cm layer. The daily and accumulated N<sub>2</sub>O fluxes, in turn, were not significantly related ( $P<0.05$ ) with the soil and climate variables herein evaluated.

4 - The vegetation seemed to have small influence on the content of mineral nitrogen in the soil, but affected the stocks of TOC and TN.

## 5. Acknowledgments

This work was supported by the Brazilian Antarctic Program through the Brazilian Council for Scientific and Technologic Development (CNPq), Foundation of Research Support in Rio de Janeiro (FAPERJ), Foundation of Research Support in Rio Grande do Sul (FAPERGS), Ministry of Environment-MMA, Ministry of Science and Technology and Inovation-MCTI and CIRM, through the National Institute of Science and Technology - Antarctic Environmental Research (INCT-APA).

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Table 1: Soil bulk density and clay, silt and sand contents for the five locals of air sampling Rip Point, Nelson Island, Antarctica.

Local	Soil Layer	Soil attribute			
		(cm)	Soil bulk density (g cm <sup>-3</sup> )	Clay content	Silt content (g kg <sup>-1</sup> )
Bare soil	0-5	1.31± 0.11	10± 10.00	334± 65.89	656± 60.82
	5-10	1.38± 0.08	13±11.54	252± 27.41	735± 32.45
	10-20	1.38± 0.08	0± 0.00	258± 51.79	742± 51.79
	20-40	1.40± 0.07	0± 0.00	254± 68.98	746± 68.98
<i>Sanionia uncinata</i>	0-5	1.11± 0.05	20± 0.00	147± 21.58	833± 21.58
	5-10	1.09± 0.05	23± 5.77	152± 10.34	824± 9.28
	10-20	1.25± 0.72	27± 5.77	150± 52.13	823± 46.36
	20-40	1.32± 0.76	23± 5.77	144± 29.62	833± 34.73
Lichen soil	0-5	1.10± 0.14	13± 5.77	199± 19.91	788± 23.63
	5-10	1.17± 0.07	30± 17.32	314± 42.75	656± 43.46
	10-20	1.15± 0.06	27± 11.54	283± 22.72	691± 34.02
	20-40	1.32± 0.76	13± 5.00	179± 21.28	816± 16.28
<i>Pasiola crispa</i>	0-5	1.16± 0.02	40± 0.00	226± 56.96	734± 56.96
	5-10	1.23± 0.04	40± 20.00	255± 60.48	705± 40.64
	10-20	1.30± 0.08	27± 11.54	235± 43.68	738± 49.55
	20-40	1.46± 0.04	20± 0.00	184± 2.92	796± 2.92
<i>Deschampsia antarctica</i>	0-5	1.13± 0.02	40± 0.00	337± 171.46	623±171.46
	5-10	1.25± 0.08	47± 11.54	168± 55.38	785± 44.77
	10-20	1.22± 0.05	29± 18.47	203± 12.35	768± 26.08
	20-40	1.53± 0.01	20± 0.00	237± 11.98	743± 11.98

Values are means ( $n = 3$ ) ± standard deviations.

Table 2: Correlation coefficient between greenhouse gases flux rates and soil and climate variables (n=18).

Flux rates		N-NH <sub>4</sub> <sup>+</sup>	N-NO <sub>3</sub>	N-NH <sub>4</sub> <sup>+</sup> +NO <sub>3</sub>	WFPS <sup>1</sup>	Soil Temperature
CH <sub>4</sub>	r	0.828	-0.012	0.748	0.187	0.167
	P	<0.001	0.959	<0.001	0.458	0.508
N <sub>2</sub> O	r	0.007	-0.007	0.004	0.054	-0.268
	P	0.977	0.976	0.985	0.829	0.283

<sup>1</sup> Water-filled pore space.

Table 3: Correlation coefficient between accumulated greenhouse gases emission and stocks of total organic carbon (TOC), particulate organic carbon (POC) and total nitrogen (TN) (n=15).

Accumulated emission	TOC stocks ( $\text{Mg ha}^{-1}$ )		POC stocks ( $\text{Mg ha}^{-1}$ )		TN stocks ( $\text{kg ha}^{-1}$ )	
	0-5 cm	0-10 cm	0-5 cm	0-10 cm	0-5 cm	0-10 cm
CH <sub>4</sub>	r	0.632	0.654	0.559	0.532	0.664
	P	<0.05	<0.01	<0.05	<0.05	<0.01
N <sub>2</sub> O	r	0.482	0.131	0.423	0.0715	0.456
	P	0.068	0.641	0.116	0.8	0.087
						0.647

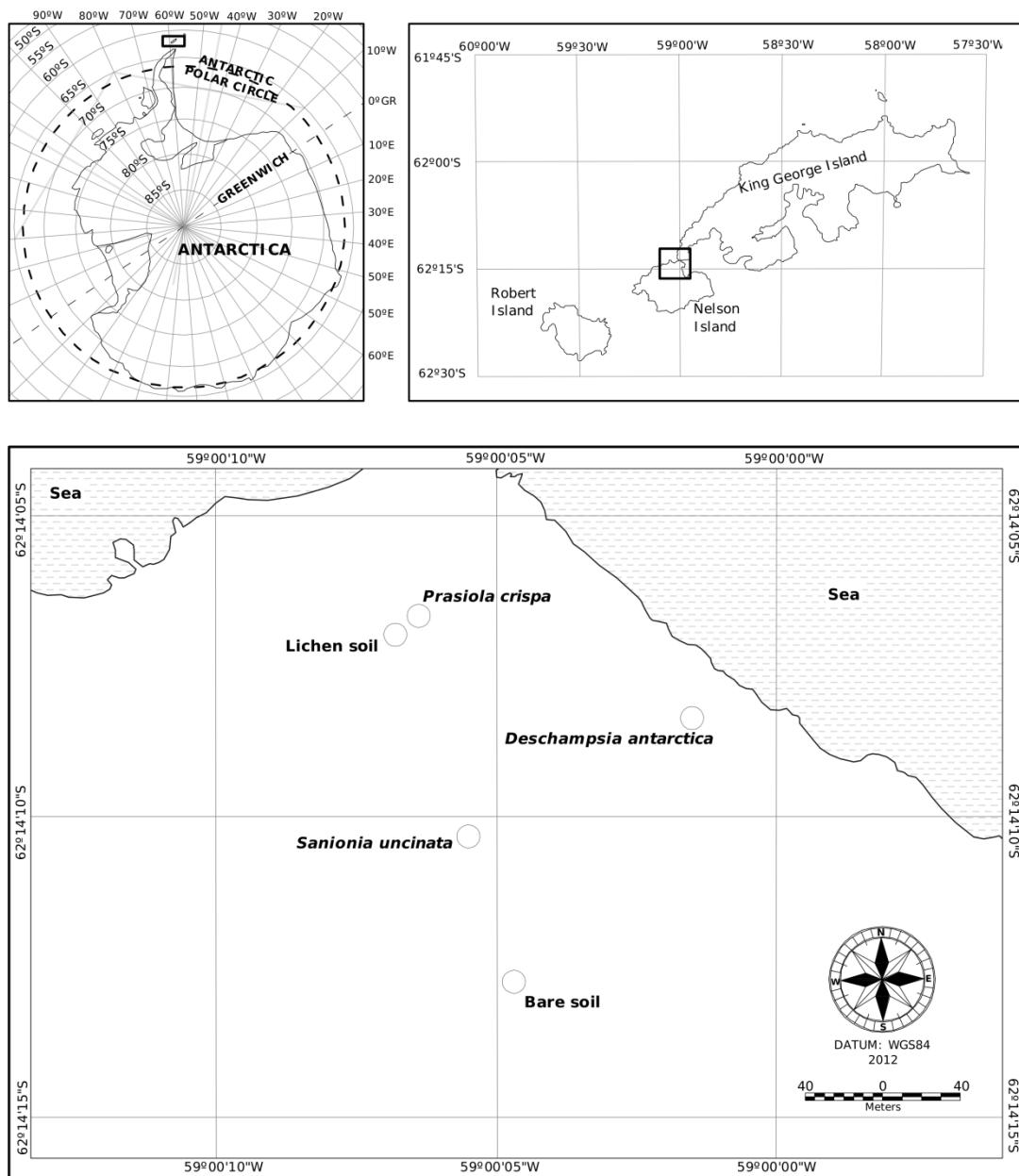


Figure 1: Location of the investigation area and sampling places in Rip Point, Nelson Island, Antarctica.

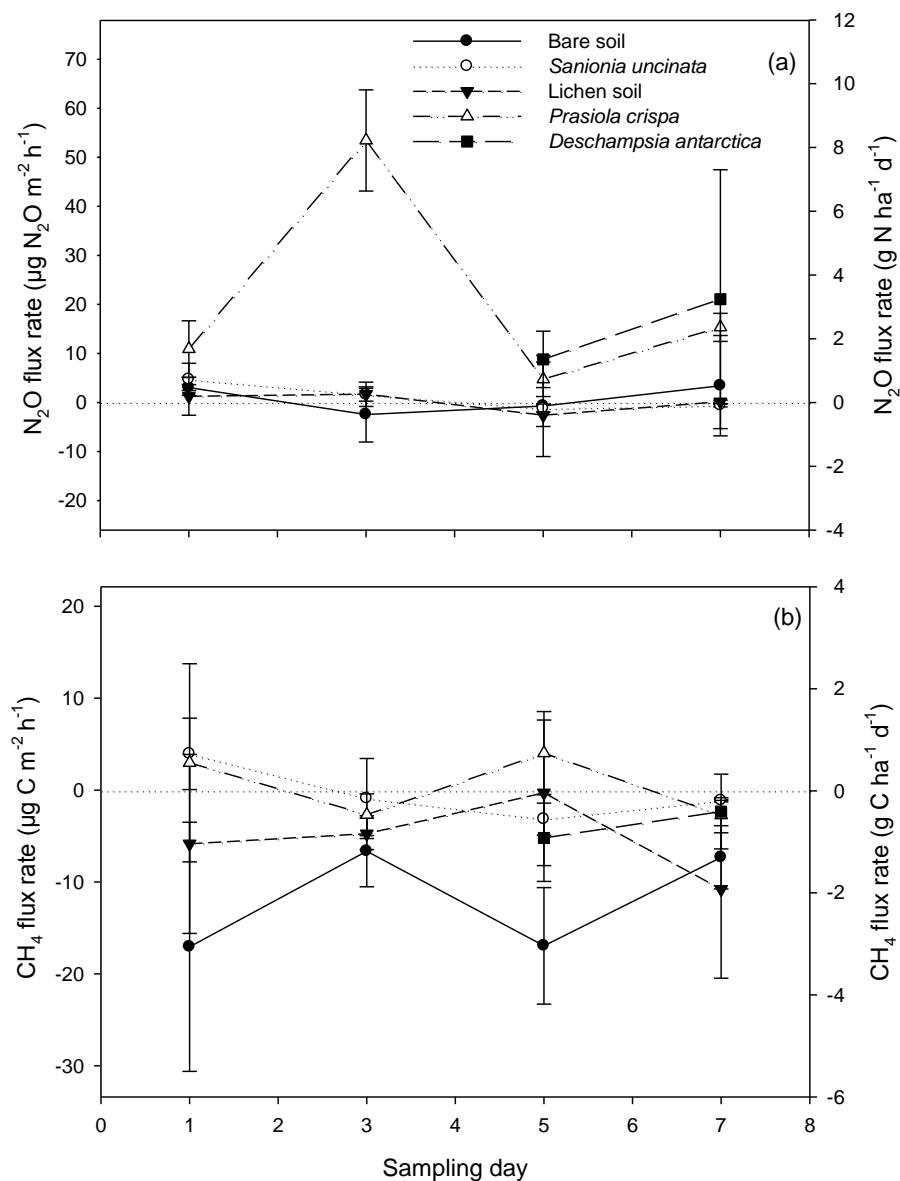


Figure 2: Rates of nitrous oxide ( $\text{N}_2\text{O}$ , a) and methane ( $\text{CH}_4$ , b) flux in soils of five areas in Rip Point, Nelson Island, Antarctica. Vertical bars mean the standard deviation of the mean ( $n=3$ ).

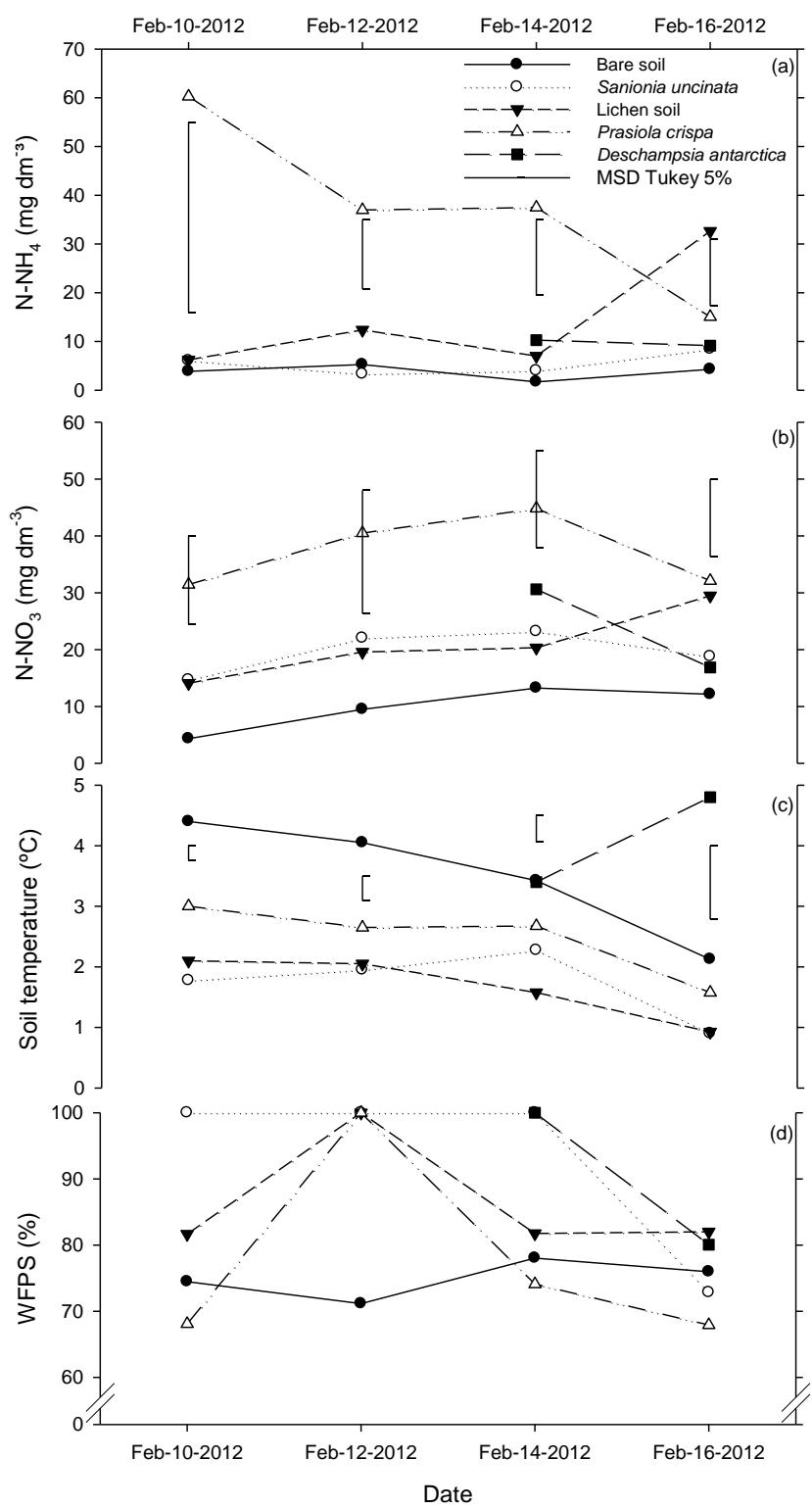


Figure 3: Mineral N contents ( $\text{NH}_4$  and  $\text{NO}_3$ ), soil temperature and Water-filled pore space (WFPS) in five areas in Rip Point, Nelson Island, Antarctica

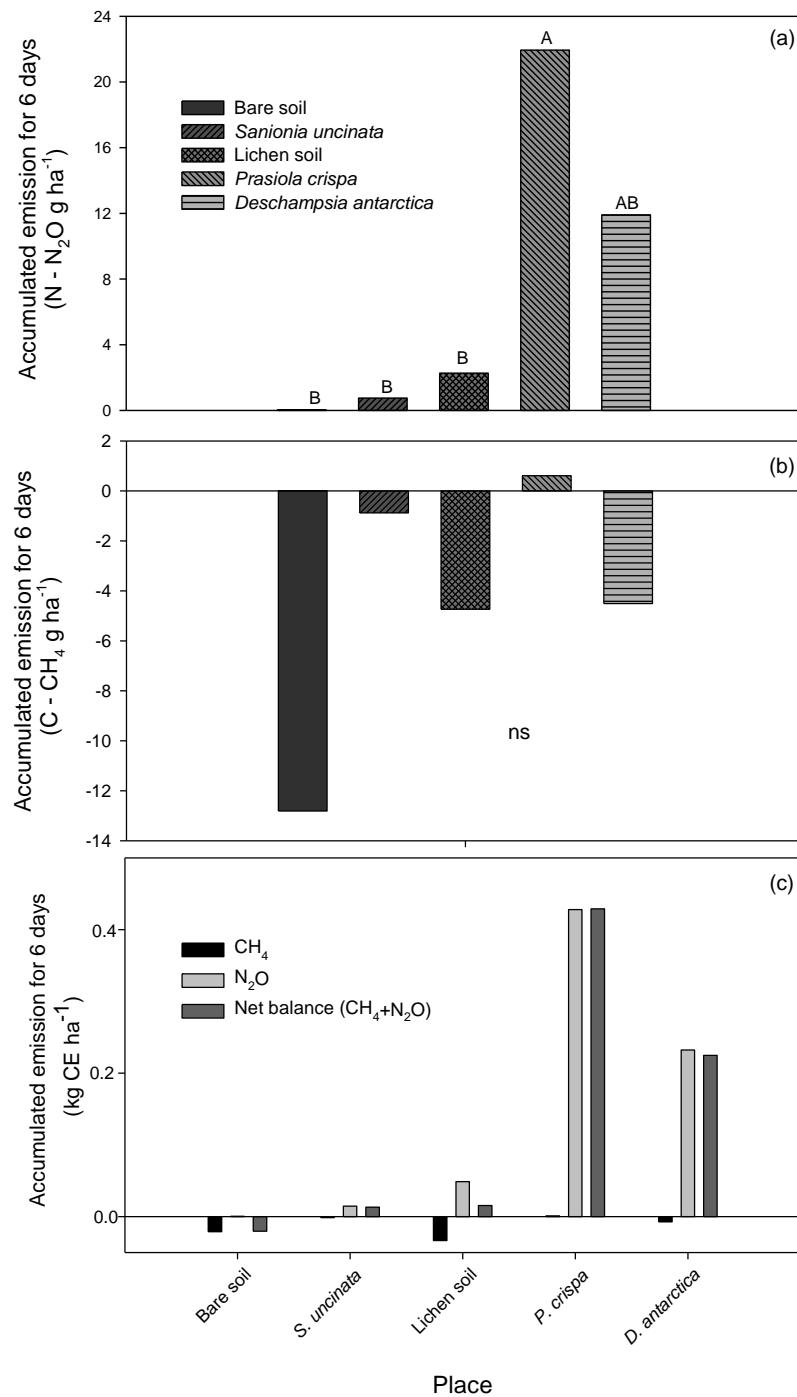


Figure 4: Accumulated emission of nitrous oxide (a) and methane (b) for six days of evaluation in soils from Rip Point, Nelson Island, Antarctica. Means followed by the same letters do not differ by Tukey test at  $P < 0.05$ . ns: not significant.

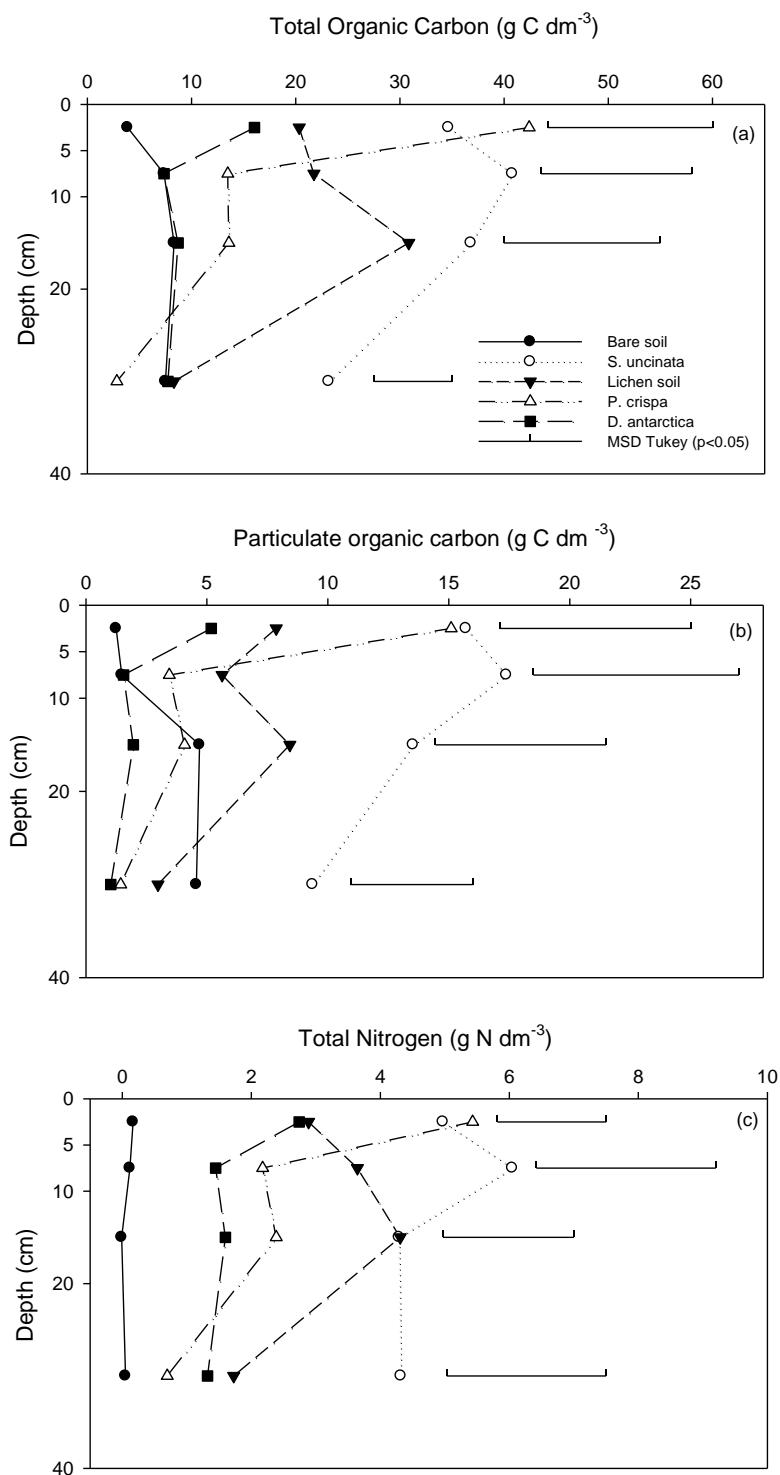


Figure 5: Soil contents of total organic carbon (a), total particulate organic carbon (b) and total nitrogen (c) in five areas in Rip Point, Nelson Island, Antarctic. Horizontal bars mean the minimum significant difference (MSD) by Tukey test at  $P<0.05$  ( $n=3$ ).

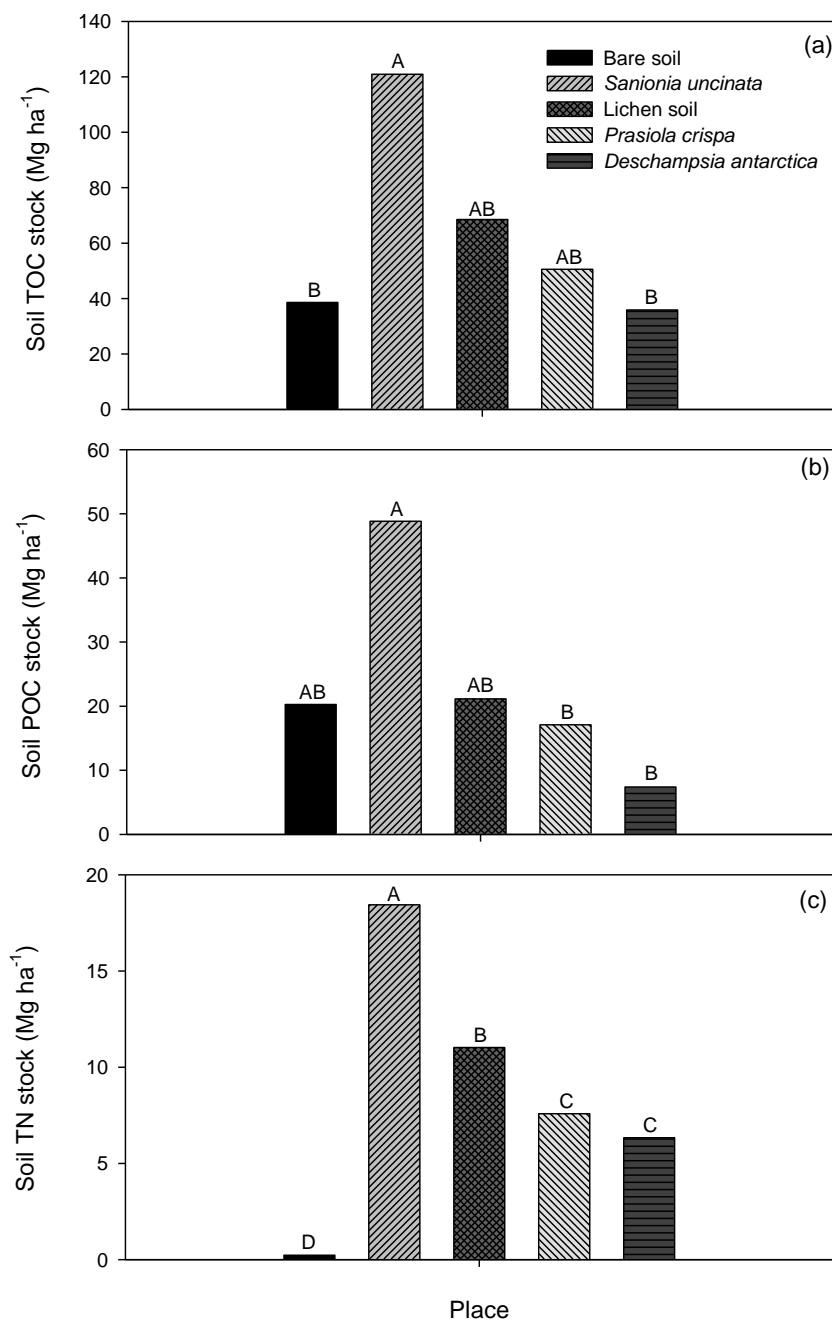


Figure 6: Soil stocks of total organic carbon-TOC (a), particulate organic carbon-POC (b) and total nitrogen-TN (c) in five areas in Rip Point, Nelson Island, Antarctic. Means followed by the same letters do not differ by Tukey test at  $P < 0.05$ .

## 6. CONCLUSÕES

1 - A atividade de aves marinhas sobre solos na Antártica marítima intensifica os fluxos de N<sub>2</sub>O.

2 - Tanto a cobertura vegetal quanto a atividade de aves marinhas podem estar influenciando os fluxos de CH<sub>4</sub>, visto que o maior potencial de absorção do gás foi observado na área de solo descoberto.

3 – Dos fatores do solo, o NH<sub>4</sub><sup>+</sup> teve correlação estatística com os fluxos diários de CH<sub>4</sub>, enquanto que os estoques de TOC, POC e TN se correlacionaram com os fluxos acumulados. Para o N<sub>2</sub>O não se obteve correlação com nenhum fator de solo e clima.

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