Universidade Federal do Rio Grande
Instituto de Ciências Biológicas
Pós-graduação em Biologia de
Ambientes Aquáticos Continentais

Influencia do uso da terra e da temperatura nos gases dióxido de carbono e metano em ecossistemas aquáticos continentais.

Leonardo Marques Furlanetto

Orientador: Dr. Cleber Palma Silva

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Tese apresentada ao Programa de Pós-graduação em Biologia de Ambientes Aquáticos Continentais como requisito parcial para a obtenção do título de Doutor em Biologia de Ambientes Aquáticos Continentais.

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Dedico aos meus Pais João e Nilza, pelo exemplo carregado de amor,
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"O que consideramos ser as pequenas coisas, são na verdade as causas das grandes coisas" (Henri-Frédéric Amiel, 1983)

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RESUMO

Os gases dióxido de carbono (CO_2) e metano (CH_4) são as principais formas na qual o carbono circula entre a litosfera, atmosfera e hidrosfera, regulados por diferentes fatores biogeoquímicos. Estes gases de efeito estufa influenciam o balanço energético e climático do planeta. Os ecossistemas aquáticos continentais destacam-se entre os principais compartimentos globais de carbono, participando como sumidouros, transportadores e fontes de CO_2 e CH_4, desta forma têm importante participação no balanço climático global. Algumas atividades antrópicas, incluindo o uso do solo e a urbanização, podem alterar o metabolismo das águas continentais e consequentemente o balanço do carbono nestes ecossistemas. Estas alterações apresentam o potencial de contribuir para o aumento do aquecimento atmosférico, e consequentemente para as mudanças nos padrões climáticos e energéticos do planeta que estão em curso. O objetivo geral desta tese foi investigar alguns fatores influenciadores do balanço dos gases de carbono em ecossistemas aquáticos subtropicais do extremo sul do Brasil. Os objetivos específicos foram : i) a influência de fatores espaciais, associados a urbanização, sobre as concentrações de CH_4 em diferentes tipos de ambientes aquáticos continentais, ii) as concentrações e taxas de produção de CO_2 e CH_4 no sedimento de áreas alagadas, iii) a mineralização do carbono orgânicos em áreas alagadas, de acordo com as projeções do IPCC de elevação da temperatura. Foram amostrados ecossistemas aquáticos localizados na planície costeira, entre os municípios de Rio Grande e Santa Vitória do Palmar. Os ambientes urbanos apresentaram concentrações mais elevadas de CH_4 na coluna da água. A entrada de matéria orgânica, a condição trófica e o tamanho dos ecossistemas, foram importantes fatores associados às maiores concentrações de CH_4. As taxas de mineralização do carbono não apresentaram diferenças significativas entres os banhados naturais e área de rizicultura. No entanto, experimentos com elevação de temperatura demonstraram uma elevação significativa destas taxas, principalmente nas áreas de rizicultura. As principais conclusões do estudo demonstram a importância de manter as características naturais das águas continentais, para que possam atuar como sumidouros, principalmente de CH_4, e que a elevação de temperatura prevista nos modelos de aquecimento global influenciarão positivamente a produção de metano.

Palavras chave: mudanças climáticas, carbono, águas continentais, matéria orgânica, rizicultura, urbanização, lagos rasos, banhados.

ABSTRACT

Carbon dioxide (CO_2) and methane (CH_4) gases are the main forms in which carbon moves through the lithosphere, atmosphere, and hydrosphere, and are regulated by different biogeochemical factors. Moreover, both are greenhouse gases and contribute to the energetic and climatic global budget. When considering the natural sources, inland waters are among the most important carbon compartments, acting as sinks, transporters, and sources of CO_2 and CH_4. Thus, these ecosystems participate considerably to global climate regulation. Anthropic activities, like land use and urbanization processes, may promote changes in the metabolism of inland waters, thus affecting the carbon gas budget. Moreover, it may affect climatic and energetic patterns, e.g. rise in atmospheric temperature. Therefore, the aim of this study was to evaluate some factors that may contribute to the carbon gas budget in subtropical aquatic ecosystems in Southern Brazil. For that, were studied: i) the influence of spatial factors associated with urbanization on CH_4 concentrations in the water column at inland waters distributed throughout urban and non-urban areas, ii) the concentrations and potential production rates of CO_2 and CH_4 from wetland sediments, and iii) the organic carbon mineralization rates in wetlands, according to IPCC projection on temperature. Field samples were taken from inland waters in the coastal plain, between the municipalities of Rio Grande and Santa Vitória do Palmar. In general, inland waters inside urban areas showed higher CH_4 concentrations in the water column, mainly the lotic ecosystem, which is surrounded by dense riparian vegetation and wetlands. The input of organic matter, trophic conditions, and the ecosystem size were important factors associated with higher CH_4 concentrations in the water column. There were no significant differences among the concentrations and rates of organic carbon production in natural and rice wetlands; however, warming promotes an elevation in mineralization rates, mainly in rice wetlands in periods of lower mean temperatures. Thus, this study showed the inherent importance of the maintenance of natural characteristics of inland waters so that these ecosystems may contribute to being a sink for carbon gases, mainly CH_4. In this way, they contribute to maintenance of the global climatic budget.

Key-words: climatic changes, carbon, inland waters, organic matter, rice crop, urbanization, shallow lakes, wetlands.

APRESENTAÇÃO

Esta tese tem como tema central o balanço de gases de carbono em ambientes aquáticos continentais da Planície Costeira do Extremo Sul Brasileiro. O texto da introdução geral, da análise do estado da arte das publicações referentes ao balanço do carbono nos ecossistemas aquáticos continentais e as considerações finais e perspectivas estão formatados de acordo com as normas da Associação Brasileira de Normas Técnicas. O restante da tese está estruturada em dois capítulos. No primeiro capítulo, o texto está formatado de acordo com as normas do periódico "**Urban Ecosystems**", para onde o manuscrito foi submetido para revisão. Neste capítulo, foram avaliadas as concentrações de metano na coluna da água de ambientes aquáticos diferenciados quanto as suas características trófica, tamanho e distribuição na paisagem (áreas urbanas e não urbanas). No segundo capítulo, o texto do artigo está formatado de acordo com as normas do periódico "**Wetlands**", onde artigo foi aceito, e encontra-se online desde Janeiro de 2018. Neste capítulo, foi avaliado experimentalmente o efeito da temperatura sobre as taxas potenciais de produção anaeróbica de dióxido de carbono e metano, em amostras de sedimento de áreas alagadas naturais e de rizicultura.

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1 INTRODUÇÃO GERAL

1.1. Os gases estufa na atmosfera

O metano (CH_4) e o dióxido de carbono (CO_2) constituem uma pequena fração da atmosfera, entretanto participam do balanço energético e climático do planeta. O CH_4 é considerado um gás em nível traço (CUNHA-SANTINO; BIANCHINI, 2013; MANAHAN, 2013), com concentrações atmosféricas estimadas em 1,804 ppm (MONTZKA; DLUGOKENCKY; BUTLER, 2011), enquanto as concentrações atuais de CO_2 são estimadas em 390 ppm. Ambos são considerados gases estufa, que promovem o aquecimento atmosférico, absorvendo na troposfera, em comprimentos de ondas específicos, a radiação infravermelha, que é refletida pela superfície terrestre na forma de calor (MANAHAM, 2013).

O potencial de aquecimento da atmosfera de um gás estufa é estimado pela sua forçante radiativa, uma variável que mede a influência de um fator sobre as entradas e saídas de energia no sistema atmosférico (IPCC, 2007). A forçante radiativa do CH_4 é cerca de 25 vezes maior em relação a forçante do CO_2 (SMITH et al., 2003; MONTZKA; DLUGOKENCKY; BUTLER, 2011). Ou seja, embora o volume do CH_4 na atmosfera seja menor em relação ao CO_2, o seu potencial de absorção da radiação infravermelha é muito superior. Desta forma, o CH_4 exerce maior influência sobre o balanço energético e climático do planeta, aquecendo a superfície terrestre (IPCC, 2007).

O CH_4 e o CO_2 são gases de carbono que circulam naturalmente através da litosfera, atmosfera e hidrosfera (CUNHA-SANTINO; BIANCHINI, 2013). As principais fontes naturais de CO_2 para a atmosfera são o intemperismo, a respiração e a decomposição (CUNHA-SANTINO; BIANCHINI, 2013), enquanto, o CH_4 é produzido naturalmente em condições anaeróbicas por grupos específicos de bactérias que vivem em habitat anaeróbicos, como o trato digestivo de ruminantes e ambientes naturais, incluindo as águas continentais (AMSTEL, 2012). Neste contexto, os ecossistemas aquático continentais são importantes sistemas naturais, que participam dos processos de produção, e emissão de gases de carbono para a atmosfera, além de serem importantes transformadores e sumidouros de carbono (BASTVIKEN et al., 2004; COLE et al., 2007).

Desde 1750, período pós-revolução industrial, as concentrações atmosféricas tanto de CH_4 como de CO_2 têm aumentado de forma significativa, atingindo nos últimos anos os níveis mais elevados em milhares de anos (Figura 1-1**Erro! Fonte de referência não encontrada.**). Algumas das principais causas diretas desta realidade são: a intensificação da produção industrial, a queima de combustíveis fósseis, e a supressão de áreas naturais (IPCC, 2014), estas causas estão associadas a necessidade de mais energia e espaço (BODELIER; STEENBERGH, 2014; MONTZKA; DLUGOKENCKY; BUTLER, 2011; LIIKANEN et al., 2006), e a intensificação da produção agrícola (AMSTEL, 2012), sendo que as áreas de rizicultura, estão entre as principais fontes de CH_4 para atmosfera (BODELIER, 2011).

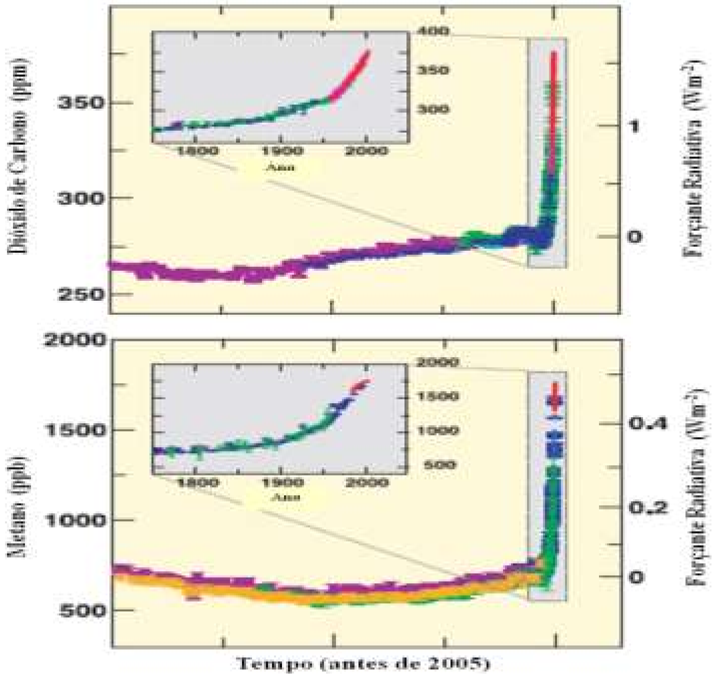

Figura 1-1: Concentrações atmosféricas dos gases CO_2 e CH_4 (eixo esquerdo) nos últimos 10.000 anos. No quadro menor estão representadas as elevações a partir do ano de 1750. O eixo da direita representa as forçantes radiativas dos gases (Fonte: adaptado de IPCC, 2014).

As projeções de mudanças climáticas devido ao aumento da emissão dos gases estufa, em um cenário de 100 anos, indicam que haverá impactos além do aquecimento atmosférico, que inclusive afetarão as áreas naturais. Na América do Sul, há previsão de elevação das taxas de precipitação e supressão de áreas naturais (IPCC, 2014). Os impactos também afetarão o metabolismo e, consequentemente, a importante participação dos ecossistemas aquáticos no balanço global do carbono (KAUSHAL et al., 2014; PODGRAJSEK et al., 2014; ROLAND et al., 2012). Serão alterados tanto os processos metabólicos relacionados à mineralização (MAROTTA et al., 2014), quanto a capacidade de participarem como fontes e sumidouros tanto de CO_2 como de CH_4 (MONTZKA; DLUGOKENCKY; BUTLER, 2011; ROLAND et al., 2012; SMITH et al., 2003).

1.2. Os gases de carbono nos ecossistemas aquáticos continentais

Todos os ecossistemas aquáticos continentais, desde os de áreas alagadas, os lênticos, e os lóticos, são importantes no balanço global do CO_2 e do CH_4. A importância de um sistema em um determinado ciclo global depende da área que este sistema ocupa na paisagem e a eficiência que transforma um elemento químico, (DOWNING et al., 2006). O desconhecimento da real distribuição dos corpos hídricos na paisagem, principalmente os sistemas pequenos (DOWNING, 2010) assim como da eficiência de transformar o carbono orgânico (COLE et al., 2007; RAYMOND et al., 2013), proporcionaram uma histórica, subestimação da real importância dos ecossistemas aquáticos continentais no balanço global do carbono. Foram por muito tempo considerados os principais sumidouros e transformadores globais de carbono exclusivamente, a atmosfera, os sistemas terrestres, e os oceânicos (COLE et al., 2007; STANLEY et al., 2015). Os ecossistemas aquáticos continentais eram vistos apenas como depósitos temporários ou elos entre os sistemas terrestres e oceânicos, no entanto, estes sistemas além de comporem a paisagem, assimilam, transformam e exportam volumes significativos de carbono. Frequentemente apresentam supersaturação de gases de carbono, mantida pelo input de carbono orgânico dos sistemas terrestres (COLE et al., 2007; RAYMOND et al., 2013). Este carbono é eficientemente transformado no sistema, podendo ser retido, transportado ou emitido para a atmosfera (ABRIL et al., 2015; INGLETT et al., 2012; MITRA; WASSMANN; VLEK, 2005; MITSCH et al., 2013).

O avanço dos estudos biogeoquímicos vinculados a distribuição geográfica das áreas alagadas, poças, lagos, lagoas e arroios, principalmente os pequenos corpos hídricos (DOWNING, 2010) promovem o reconhecimento da importância dos ambientes aquáticos continentais no balanço global do carbono (STANLEY et al., 2015). As estimativas recentes apontam que o estoque de carbono orgânico nos solos são de ~4000Tg C, dos quais uma fração substancial é carreada para os ecossistemas aquáticos 0,022 Gt C (22 Tg C) onde é processada e emitida para atmosfera (PREMKE et al., 2016). A importante participação no balanço do carbono está relacionada com a capacidade dos ecossistemas aquáticos continentais transformarem volumes significativos de carbono, em uma área proporcionalmente menor em relação aos sistemas terrestres e oceânicos (COLE et al., 2007; DOWNING, 2010; MEGONIGAL; HINES; VISSCHER, 2004). Os sistemas lóticos, anteriormente considerados apenas como transportadores de matéria, são eficientes nas transformações do carbono; principalmente os de origem terrestre. Estudos de MASSICOTTE et al., (2017), demonstraram que o carbono é transformado em formas menos reativas, a partir de áreas de planícies alagadas, passando por sistemas lóticos até chegar nos oceanos. Ao longo deste contínuo de ecossistemas, o carbono total é perdido, passando por transformações mais significativas, em relação ao nitrogênio, fósforo, ferro e sílica (WEYHENMEYER; CONLEY, 2017). No decorrer destas transformações, volumes consideráveis do carbono orgânico são mineralizados e emitidos para a atmosfera, nas formas de CH_4 e CO_2 (MASSICOTTE et al., 2017; NATCHIMUTHU; PANNEER SELVAM; BASTVIKEN, 2014; STANLEY et al., 2015).

A eficiência nos processos de produção primária, respiração e atividades microbianas, tanto aeróbicas quanto anaeróbicas são determinantes no balanço do carbono (MEGONIGAL; HINES; VISSCHER, 2004). Os ecossistemas aquáticos continentais são frequentemente sistemas heterotróficos, onde a respiração excede a produção primária, promovendo a saturação de gases, por exemplo o CO_2, que advém da respiração do carbono orgânico (RAYMOND et al., 2013). As transformações têm início a partir da incorporação do CO_2 atmosférico, via produção primária e seguem ao longo dos diferentes processos metabólicos, culminando com a produção de CO_2 e CH_4 (ESTEVES; MARINHO, 2011; SMITH et al., 2003). As entradas, incorporação e deposição do carbono orgânico no sedimento viabiliza a mineralização (CASPER, 1992; BASTVIKEN et al., 2004; MOZETO, 2004 ESTEVES; MARINHO, 2011), estes fatores associados a concentração de oxigênio determinam se o sistema aquático atuará como fonte e/ou sumidouro de carbono (BODELIER; LAANBROEK, 2004; CLAYER et al., 2016). A coluna da água limita e regula a disponibilidade de oxigênio no sedimento assim como as trocas com a atmosfera (FORD; BOON; LEE, 2002; MEGONIGAL; HINES; VISSCHER, 2004). No sedimento, o oxigênio regula as taxas de mineralização do carbono orgânico (MAROTTA et al., 2014) e a capacidade do sedimento atuar como fonte ou sumidouro de carbono (SOBEK et al., 2017).

As concentrações, taxas de produção, consumo e fluxos para a atmosfera variam de acordo com o tipo de ambiente aquático, lêntico ou lótico. Mas alguns fatores são preponderantes, dentre estes as entradas e deposição de matéria orgânica. Quando a deposição de matéria orgânica no sedimento excede as saídas, o sistema atua como sumidouro de carbono (

Figura **1-2**), acumulando a biomassa nos detritos (BODELIER; LAANBROEK, 2004; BODELIER, 2011) e nas formas inorgânicas, que abrange o CO_2 e o CH_4 (KORTELAINEN et al., 2006). Quando as entradas se equivalem às saídas, os ecossistemas participam como transformadores via fotossíntese e respiração (aeróbica e anaeróbica). Por fim, quando as saídas excedem as entradas e a incorporação na biomassa, os sistemas atuam como fontes de carbono (MITSCH; GOSSELINK, 2015), emitindo (CO_2, CH_4) os produtos do metabolismo para a atmosfera (COLE et al., 2007; SMITH et al., 2003).

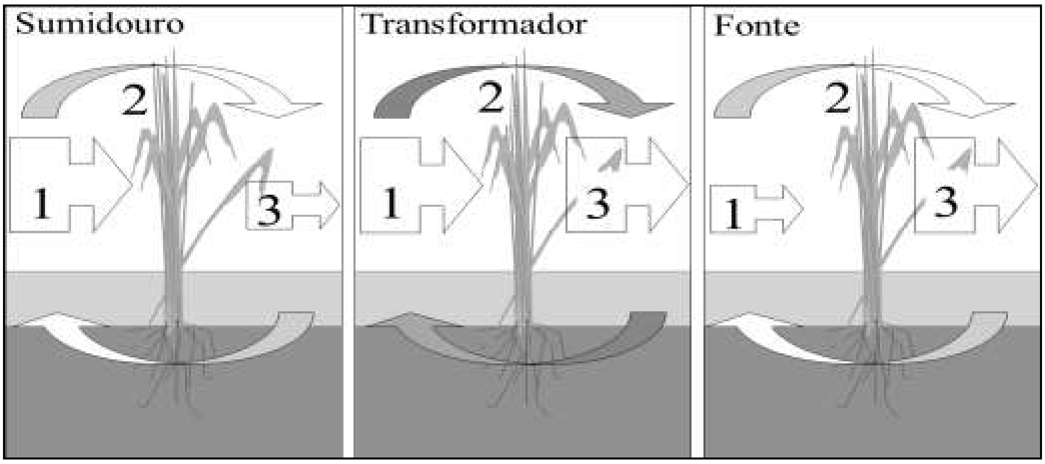

Figura 1-2: Ecossistemas aquáticos atuando como sumidouros, transformadores e fontes de carbono orgânico (exemplo de áreas alagadas). Os números representam: 1- entradas, 2 – transformações, 3 – saída do carbono nos ecossistemas aquáticos. As caixas e setas representam as entradas e saídas em maiores ou menores concentrações, de acordo como o tamanho da caixa. Fonte: adaptado de MITSCH; GOSSELINK, 2015, proposto para áreas alagadas.

1.2.1. *Entradas*

Os processos autóctones (excreção, autólise, decomposição microbiana dos detritos) e os inputs alóctones são as principais fontes de carbono orgânico para os ecossistemas aquáticos continentais (CUNHA-SANTINO; BIANCHINI, 2013;

WESTON et al., 2014). As contribuições alóctones e autóctones variam temporal e espacialmente em lagos, e controlam o acúmulo de carbono no sedimento (HUANG et al., 2017). Os processos de fotossíntese e quimiossíntese incorporam carbono inorgânico oxidado (CO_2) e transformam em compostos orgânicos reduzidos. A matéria orgânica produzida via produção primária bruta (PPB), suporta o processo de respiração e transformações do carbono desde os organismos autótrofos até os heterótrofos (ESTEVES et al., 2011; MITSCH; GOSSELINK, 2015). O carbono não mineralizado, produção primária líquida (PPL), acumula na biomassa dos níveis tróficos superiores e/ou é transformada em detrito, que fica estocado no sedimento (COLE et al., 2007; ESTEVES et al., 2011). As camadas superficiais do sedimento acumulam volumes maiores de carbono orgânico da biomassa ecossistêmica, principalmente da produção primária (MEGONIGAL et al., 2004).

O material de origem alóctone, oriundo principalmente da vegetação ripária, é uma fonte substancial de detritos em sistemas lóticos (MASSICOTTE et al., 2017; NATCHIMUTHU et al., 2017; STANLEY et al., 2015). Os detritos alóctones favorecem o aumento das concentrações de nutrientes no sedimento, viabilizando a produção primária (FURLANETTO et al., 2012), e emissões de CO_2 (MAGIN et al., 2017). Tanto os detritos alóctones como os autóctones servem de substrato para mineralização do carbono orgânico (BASTVIKEN et al., 2004; COLE et al., 2007; FURLANETTO et al., 2012), cujo produto final pode ser o CH_4 (AMSTEL, 2012; STANLEY et al., 2015).

1.2.2. *Transformações*

O CH_4 é o principal produto do metabolismo anaeróbico (ZINDER, 1993), enquanto o CO_2 é o principal produto do metabolismo aeróbico (COLE et al., 2007; STANLEY et al., 2015) e ambos são produtos de transformações microbianas associadas a mineralização do carbono orgânico. A produção de CH_4 (metanogênese) domina a mineralização do carbono orgânico nos compartimentos anaeróbicos, ocorrendo principalmente no sedimento (MEGONIGAL et al., 2004; SAUNOIS et al., 2016), onde o CO_2 também pode ser produzido, no entanto, será reduzido a acetato e CH_4 (BODELIER; STEENBERGH, 2014; LIIKANEN; MURTONIEMI; TANSKANEN, 2002). A metanogênese é realizada por um grupo de bactérias extremamente especializadas (metanogênicas), pertencentes ao filo Euryarchaeota, domínio Archaea (BODELIER; STEENBERGH, 2014). As bactérias metanogênicas, em sua maioria, utilizam compostos contendo apenas um ou dois carbonos (ZINDER, 1993). A obtenção de compostos simples para a metanogênese depende de interações tróficas (SCHILDER et al., 2017), e da atividade de outros grupos de bactérias, que produzem subtratos com menor peso molecular (MEGONIGAL et al., 2004; KELLER et al., 2009). A disponibilidade destes substratos está ligada a qualidade da matéria orgânica, o principal fator limitante para a metanogênese (BODELIER; STEENBERGH, 2014; SEGERS, 1998).

A concentração de oxigênio, principal aceptor terminal de elétrons, é outro fator essencial (FORD et al., 2002). A disponibilidade dos elementos oxidantes diminuem as concentrações de oxigênio, da coluna da água em direção as camadas mais profundas do sedimento (ESTEVES; MARINHO, 2011). Os aceptores de elétrons mudam com o estabelecimento da anaerobiose, sendo estes, em ordem de decaimento (Figura 1-3): o NO_3 (desnitrificação), Fe^{+3} (Ferro redução), Mn^{+4} (redução do manganês) e SO_4^{-2} (sulfato redução), CO_2 e metanogênese (BANGE, 2006; MARINHO et al., 2009; BROUNS et al., 2014). Ou seja, a supressão dos aceptores de elétrons mais favoráveis está associada a produção de CH_4 (BODELIER; STEENBERGH, 2014), mas a presença destes aceptores pode inibir a metanogênese, devido a competição por substratos, como no caso da sulfato redução (MARINHO et al., 2009).

O processo metanogênico tem início com a degradação dos detritos orgânicos, polímeros e monômeros naturais (Figura 1-3), que são inicialmente transformados por reações de hidrólise e fermentação (BODELIER, 2011; FORD; BOON; LEE, 2002; LIIKANEN; MURTONIEMI; TANSKANEN, 2002). Os materiais autóctones e alóctones são transformados em moléculas mais simples, com menor peso molecular, produzindo CO_2, hidrogênio (H_2), acetato (CH_3CO_2) e álcoois (i.e.: metanol), os principais substratos para produção de CH_4 (BASTVIKEN et al., 2004; MEGONIGAL; HINES; VISSCHER, 2004). Simplificadamente, a produção de CH_4 pode ocorrer por três vias (Figura 1-3). A primeira é a via hidrogenotrófica, onde as bactérias metanogênicas utilizam moléculas mais simples para obter energia, a partir do H_2 + CO_2, reduzindo o CO_2 e oxidando o H_2 para produzir CH_4. A segunda é pela via acetoclástica, onde o acetato é utilizado para produzir o CH_4 , e a na terceira, chamada de via metilotrófica, o metanol e metilaminas são os substratos para a produção de CH_4 (BODELIER; STEENBERGH, 2014). Normalmente as bactérias metanogênicas possuem apenas uma das vias, apesar de algumas espécies (*Methanosarcina*) terem a capacidade de produzir CH_4 pelas três vias (ZINDER, 1993).

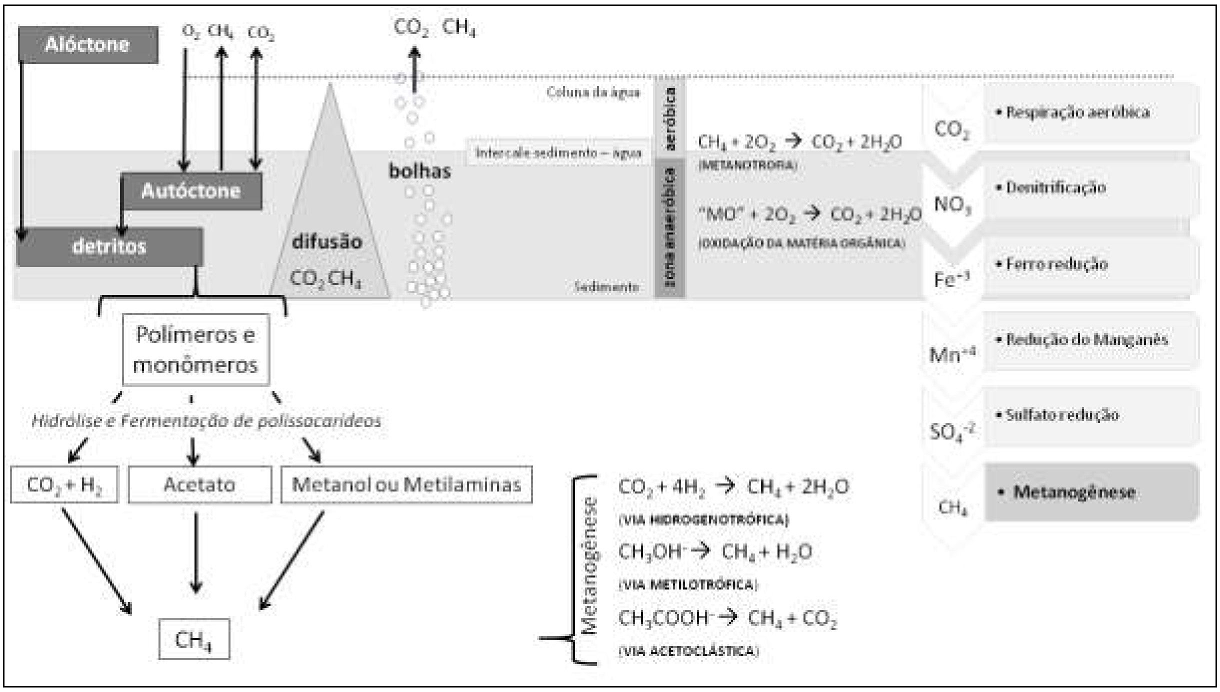

Figura 1-3: Representação esquemática das transformações do carbono e dos principais processos de entrada e saída (difusão e ebulição) do carbono nos sistemas aquáticos. Esquema genérico da metanogênese, e processos associados aos compartimentos aeróbicos e anaeróbicos, bem como dos principais substratos e as vias da respiração anaeróbica, com utilização do CO_2 como aceptor de elétrons, aceptores com menor peso molecular, vias de produção e consumo de CH_4 ou produção de CO_2. (Fonte: adaptado de ESTEVES, 2011)

O balanço entre a metanogênese e a metanotrofia (Figura 1-3) determina se o sedimento retém ou libera CH_4 (BODELIER; LAANBROEK, 2004). Pequenas variações nos níveis de oxigênio podem alterar significativamente as taxas de mineralização da matéria orgânica e consequentemente o balanço do CH_4 (CLAYER et al., 2016). Nos compartimentos aeróbicos, o metano serve de recurso para a metanotrofia, ou o consumo de CH_4, realizado pelas bactérias metanotróficas (ZINDER, 1993; SCHILDER et al., 2017), que ocupam os compartimentos oxigenados, geralmente a interface sedimento-água dos ambientes aquáticos (BODELIER; LAANBROEK, 2004; ESTEVES et al., 2011). A metanotrofia pode ser o principal sumidouro do CH_4 no sedimento (BODELIER, 2011), entretanto, a deposição de matéria orgânica, a condição anóxica, e a metanogênese fazem do sedimento uma importante fonte de CH_4 (BODELIER, 2011; CLAYER et al., 2016), que pode ser emitido para atmosfera (ZINDER, 1993). O balanço entre as taxas de decomposição e oxidação do carbono determinam as concentrações do CO_2 e CH_4 no sedimento e na coluna da água, bem como as taxas de difusão entre estes compartimentos, e também as emissões para a atmosfera (BASTVIKEN et al., 2004; PALMA-SILVA et al., 2013).

1.2.3. *Emissões*

A mineralização anaeróbica influencia as taxas de emissão do CH_4, enquanto a oxidação do CH_4 e a respiração nos compartimentos aeróbicos regulam a emissão de CO_2 (COLE et al., 2007). Quando as taxas de respiração ecossistêmicas excedem a produção primária bruta, os produtos da mineralização do carbono orgânico ficam supersaturados, situação que favorece as trocas entre os compartimentos mais concentrados para os menos concentrados. Desta forma, a supersaturação dos gases na superfície da coluna da água favorece a emissão para a atmosfera (NATCHIMUTHU et al., 2014; STANLEY et al., 2015; STURM et al., 2014). Segundo BASTVIKEN et al., (2004), as emissões a partir dos ambientes aquáticos podem ocorrer por pelo menos quatro vias: difusão, bolhas, macrófitas emergentes, e via estoques.

A difusão (Figura 1-3) depende da supersaturação dos gases no sedimento, que difundem para a coluna da água, até serem emitidos para a atmosfera de entorno por diferença de concentração (PODGRAJSEK et al., 2014). Quando a pressão parcial do gás (pCO_2 ou pCH_4) na coluna da água é menor do que a pressão da pressão do gás na atmosfera, o ecossistema atua como fonte de gás para a atmosfera (MAGIN et al., 2017). A emissão por bolhas (Figura 1-3), ou ebulição, também depende da supersaturação no sedimento (MARINHO et al., 2004; PALMA-SILVA et al., 2013), neste caso os gases são liberadas direto do sedimento para a atmosfera. As bolhas são eventos esporádicos, que minimizam a oxidação do CH_4 na coluna da água (BASTVIKEN et al., 2004). Em um trabalho experimental com incubações de sedimento de um lago, pós eutrofização, SCANDELLA et al., (2017) demonstraram potencial predomínio de CH_4 (83%) na composição da massa de gás emitido por ebulição do sedimento.

As plantas aquáticas emergentes transportam os gases via aerênquima, e desta forma emitem os gases do sedimento para a atmosfera (BASTVIKEN et al., 2004). Nas planícies de inundação amazônicas em períodos de alagamento, as árvores e macrótitas emergentes são responsáveis pelas maiores taxas de emissão de CH_4 (PANGALA et al., 2017). As macrófitas podem também oxigenar o sedimento, principalmente no entorno das raízes, favorecendo a oxidação do CH_4 (BODELIER, 2011). A emissão por estoques é positivamente correlacionada com a condição anóxica. Este tipo de emissão prevalece em sistemas mais produtivos, com concentrações elevadas de fósforo, assim como lagos estratificados ou reservatórios profundos de hidroelétricas. Os estoques também apresentam correlação positiva com a área do sistema (m^2). Os sistemas com elevados estoques de CH_4 em zonas anóxicas, apresentam elevadas trocas coluna da água - atmosfera (BASTVIKEN et al., 2004).

Os ambientes aquáticos participam significativamente do balanço global dos gases estufa, e estão entre as fontes mais importantes de carbono para a atmosfera (BASTVIKEN et al., 2011; COLE et al., 2007; RAYMOND et al., 2013; TRANVIK et al., 2009). As taxas de emissão podem ser semelhantes as taxas de produção dos ecossistemas terrestres, e ao sequestro de carbono orgânico no fundo dos oceanos (TRANVIK et al., 2009). As estimativas de BASTVIKEN et al., (2011) considerando a distribuição global das águas continentais, demonstraram que a emissão de CH_4 a partir dos ambientes aquáticos pode chegar a 103 Tg/CH_4 ano^{-1}, que corresponde a 0,65 Pg/C (CO_2 eq) ano^{-1}. Estes valores somados as estimativas de emissão de CO_2 (1,4 Pg C (CO_2 eq) ano^{-1}), corresponde a 79% do sequestro de gases estufa na superfície terrestre (BASTVIKEN et al., 2011).

1.3. O clima, os ambientes aquáticos e o homem

A biosfera é uma rede interligada e metabolicamente ativa, onde a participação dos ecossistemas aquáticos é cada vez mais preponderante (DOWNING, 2010). Como foi apresentado nos itens anteriores, os processos ecossistêmicos relacionados ao balanço dos gases de carbono regulam seu ciclo nos ambientes aquáticos. Estes processos sofrem influência de fatores climáticos, assim como também podem influenciar os processos climáticos (BRIDGHAM et al., 2006; DOWNING, 2010; KELLER; WEISENHORN; MEGONIGAL, 2009; ROLAND et al., 2012; SAUNOIS et al., 2016; THORNTON et al., 2014). As altas taxas de produção e emissão de CO_2 e CH_4 para a atmosfera, a partir dos ecossistemas aquáticos podem contribuir de forma positiva com os processos de mudanças climáticas. Por outro lado, podem mitigar o aumento das concentrações de gases estufa quando atuam com sumidouros de gases estufa (BRIDGHAM et al., 2006; ROLAND et al., 2012), entretanto estas características de atuar como fontes e/ou sumidouros de carbono é influenciada pela ação antrópica (ROLAND et al., 2012; STURM et al., 2014).

Os principais fenômenos relacionados às mudanças climáticas, observados nas últimas décadas, são consequência direta de atividades humanas, cuja a forçante radiativa está relacionada com o aumento da emissão de gases estufa (IPCC, 2014). Algumas atividades humanas utilizam os serviços ecossistêmicos a ponto de sucumbir os ambientes aquáticos da paisagem, por exemplo a agricultura e a urbanização (BRIDGHAM et al., 2006; NISBET et al., 2014). Como consequência, além das emissões diretas, as atividades humanas que alteram os serviços ecossistêmicos, afetam de forma indireta o balanço dos gases estufa.

Para determinar a real influência do homem sobre os processos ecossistêmicos e climáticos, bem como sobre os *feedbacks* positivos e negativos entre estes compartimentos, ainda é necessário avançar o conhecimento. Desta forma será possível o desenvolvimento de estratégias voltadas a mitigar os impactos antrópicos sobre os processos ecossistêmicos (ROLAND et al., 2012, STANLEY et al., 2016; MASSICOTTE et al., 2017). Minimizando as emissões de gases, assim como seus efeitos sobre os processos climáticas (BANGE, 2006). Para avançar no conhecimento ecológico, relacionado aos processos e fatores que afetam a produção e o consumo dos gases estufa, há lacunas a serem preenchidas, tanto em nível de processos ecossistêmicos como climáticos

A temperatura é um fator climático preponderante para os processos ecossistêmicos (ROLAND et al., 2012; THORNTON et al., 2014), regula a intensidade do metabolismo, que inclui o balanço do carbono (FORD et al., 2012; SCHULZ; CONRAD, 1996). O aumento da temperatura eleva exponencialmente as taxas de mineralização do carbono orgânico (AGREN; WETTERSTEDT, 2007; MAROTTA et al., 2014; NATCHIMUTHU et al., 2017), e as emissões de CO_2 e CH_4 (BASTVIKEN et al., 2004; PALMA-SILVA et al., 2013). Além do mais, a temperatura regula a retenção do carbono no sedimento, sem significativas variações em gradientes latitudinais (SOBEK et al., 2017). Em regiões boreais WEYHENMEYER; CONLEY (2017) encontraram transformações do carbono inorgânico dissolvido na coluna da água mais significativas, quando associadas a variação sazonal da temperatura (inverno-verão), que as transformações vinculadas ao contínuo de ecossistemas aquáticos, desde as águas continentais até as zonas costeiras.

As emissões a partir de fontes naturais estão entre as maiores fontes de incerteza relacionadas ao aumento das concentrações atmosféricas de CH_4 (SAUNOIS et al., 2016) e demais gases estufa. Um terço das emissões de CH_4 provém de fontes naturais, e as atividades humanas contribuem para o aumento destas emissões (NISBET et al., 2014). Além das atividades humanas, a deposição atmosférica e a hidrologia, também são fatores preponderantes no balanço do carbono nos ecossistemas aquáticos (WEYHENMEYER; CONLEY, 2017). Apesar dos avanços no conhecimento, ainda há necessidade de identificação de zonas favoráveis a produção e emissão de gases estufa (BANGE, 2006; NATCHIMUTHU et al., 2017) e transformações do carbono ao longo da paisagem, desde a superfície terrestre até os oceanos (COLE et al., 2007; MASSICOTTE et al., 2017; WEYHENMEYER; CONLEY, 2017; HUANG et al., 2017). Este estudo contribui para elucidar os processos relacionados às transformações do carbono nas águas continentais na planície costeira do Rio Grande do Sul.

2 O ESTADO DA ARTE DAS PUBLICAÇÕES REFERENTES AO BALANÇO DO CARBONO NOS ECOSSISTEMAS AQUÁTICOS CONTINENTAIS

Os ecossistemas aquáticos apresentam, frequentemente, condição supersaturada de gases de carbono, tanto no sedimento como na coluna da água, devido aos processos ecossistêmicos e a integração com o entorno (MASSICOTTE et al., 2017; NATCHIMUTHU et al., 2017; SAUNOIS et al., 2016; STANLEY et al., 2015). Estas são algumas das condições que inserem os ambientes aquáticos continentais entre as principais fontes naturais de carbono para atmosfera, ~1,8 Pg C ano^{-1} (RAYMOND et al., 2013). Ao mesmo tempo, as principais fontes de estão associadas aos ambientes aquáticos, como por exemplo, as emissões de CH_4 (SAUNOIS et al., 2016).Estudos de revisão e modelagem têm demonstrado a importância das emissões de carbono a partir das águas continentais (BORGES et al., 2015; COLE et al., 2007; RAYMOND et al., 2013). Outras pesquisas indicam que a compreensão da contribuição destes ecossistemas no balanço global do carbono, passa pelo preenchimento de lacunas, principalmente as relacionadas às diferenças entre os tipos de sistemas aquáticos (áreas alagadas, lênticos e lóticos), a sua distribuição na paisagem, bem como quanto aos volumes emitidos (HOLGERSON; RAYMOND, 2016; MASSICOTTE et al., 2017; MENDONÇA et al., 2017; XENOPOULOS et al., 2017). As estimativas de (RAYMOND et al., 2013), para as emissões globais de CO_2 referem-se principalmente a ecossistemas do sul e leste Asiático, Amazônia, América Central, Europa, Sul do Alaska e ao Oeste Africano. No que diz respeito as emissões de CH_4, a distribuição global ainda é pouco conhecida, como é apontando por (BORGES et al., 2015).

Para revisar os estudos científicos relacionados ao balanço do carbono nas águas continentais foi realizada uma busca na base de dados da "*Web of Science*", dos artigos publicados entre os anos de 1945 e 2017, utilizando a seguinte combinação de palavras-chave: "*carbon budget**" e "*carbon dioxide**" e "*methane*" e "inland water*" ou "freshwater*". Nestas publicações, foram analisados o título e resumo para identificar a presença das seguintes informações: o tipo de ecossistema estudado, a forma de carbono e a região climática onde o estudo foi realizado.

Na primeira busca foram encontradas um total de 2886 publicações, das quais prevaleceram estudos relacionados à biodiversidade, principalmente associada as comunidades fitoplanctônica e de peixes. Outra parte das publicações avaliaram processos ecológicos, principalmente relacionados ao input de nutrientes, a contaminantes e águas residuais. Após a análise do título e resumo, foram encontradas 281 publicações que estudaram aspectos relacionados ao balanço do carbono e gases CO_2 e CH_4 em ecossistemas aquáticos continentais. A análise da distribuição temporal destas publicações indica número crescente de artigos publicados nos últimos anos. É observado que após o ano de 2009, ocorreu um aumento exponencial do número de publicações, passando de 4 para 88 artigos até o ano de 2017 (Figura 2-1).

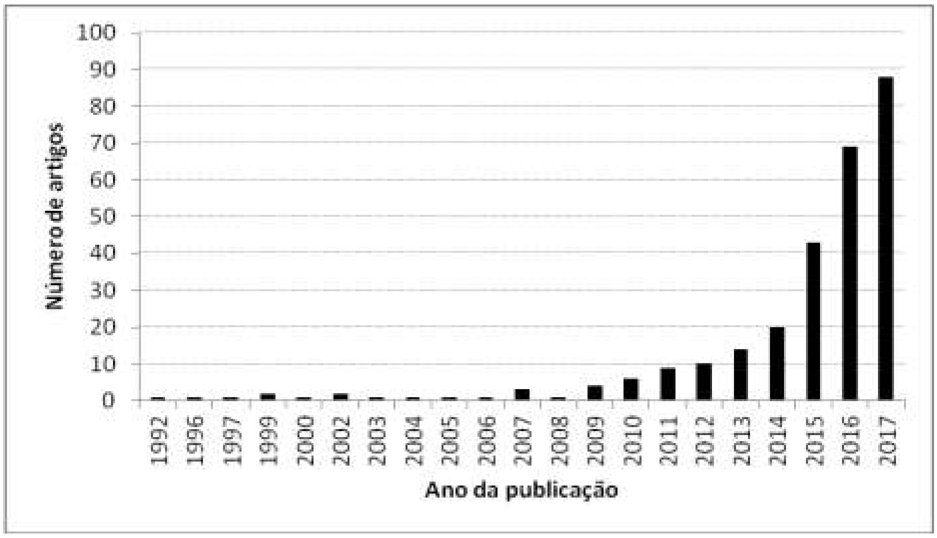

Figura 2-1: Número de publicações por ano, que abordam diferentes etapas do balanço do carbono em ecossistemas aquáticos continentais.

A avaliação do tipo de ecossistema estudado demonstra que os lagos foram os principais ecossistemas aquáticos investigados (34%), seguido pelos sistemas lóticos. Os trabalhos voltados a investigação de mais de um tipo de ecossistema aquático, ou que avaliaram as transformações do carbono durante o transporte desde áreas alagadas até zonas costeiras representam 20% das publicações (Figura 2-2).

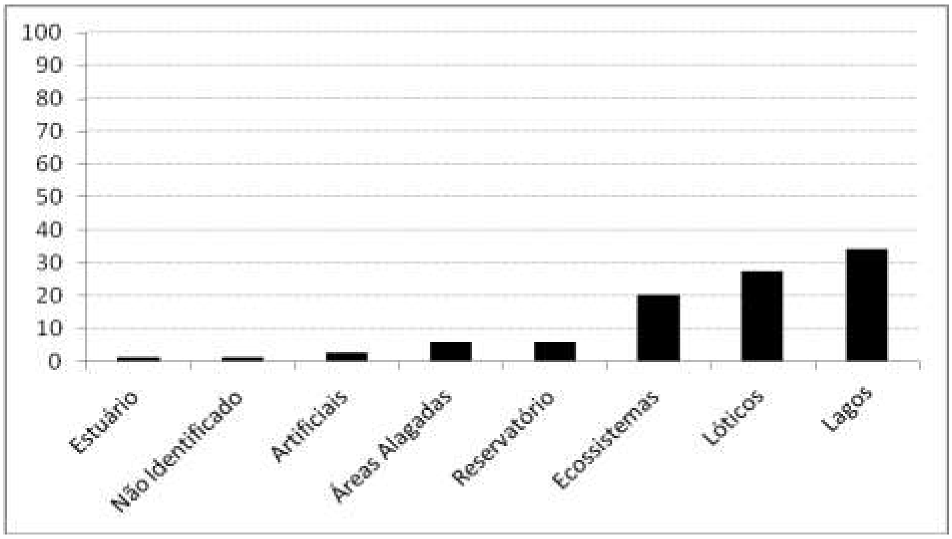

Figura 2-2: Proporção dos tipos de ecossistemas investigados nas 281 publicações. O termo ecossistemas refere-se ao percentual de artigos que investigaram mais de um tipo de ambiente aquático (áreas alagadas, lóticos, lênticos) ou transformações do carbono ao longo de contínuos.

A avaliação da forma de carbono investigada (Figura 2-3) verificou que o maior percentual das publicações estudou aspectos relacionados ao balanço do CO_2 (34%). O segundo maior percentual está relacionando a estudos das formas de carbono que abrangem as concentrações de carbono orgânico total, particulado, dissolvido e/ou inorgânico. O percentual de publicações que avaliaram ambos os gases CO_2 e CH_4, foi de 18%.

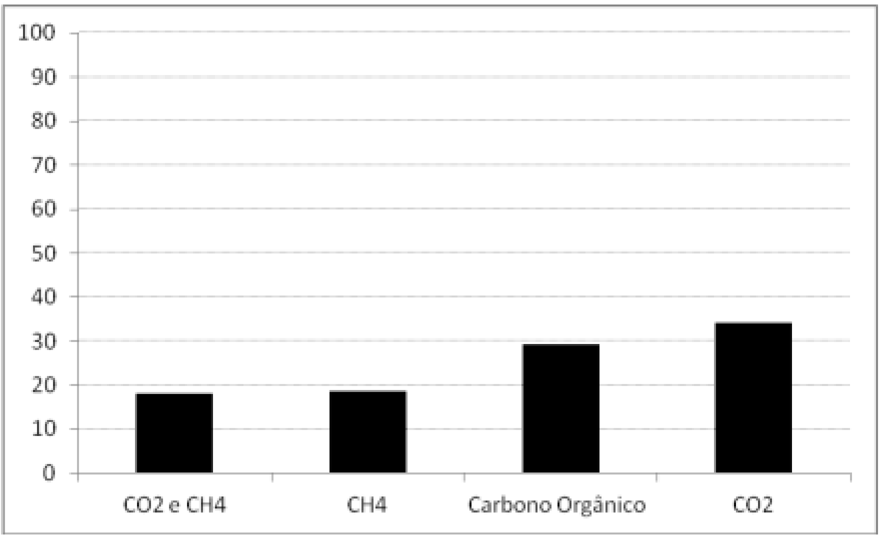

Figura 2-3: Proporção das formas de carbono investigadas nos 281 artigos publicados. O termo carbono, abrange as formas de carbono orgânico dissolvido, particulado, inorgânico e total.

Utilizando os mesmos artigos constatou-se que na distribuição geográfica (Figura 2-4), há predomínio de publicações no continente europeu (28%). Do total de 69 publicações no continente europeu, 3 são comparações com ecossistemas do continente Sul Americano, em regiões tropicais. A Oceania e a África apresentaram os menores percentuais de publicações, corroborando BORGES et al., (2015), que ressaltaram a carência de informações em relação ao continente africano.

A avaliação do percentual de publicações por região climática (Figura 2-5), revela um predomínio de publicações realizadas nas regiões temperadas (43%), seguido pelas áreas tropicais e subtropicais. Na região subtropical, observa-se uma significativa proporção de trabalhos realizados na China e apenas dois trabalhos realizados na região subtropical Brasileira, realizado em Santa Catarina. A combinação de palavras chave não encontrou publicações realizados no extremo sul do Brasil.

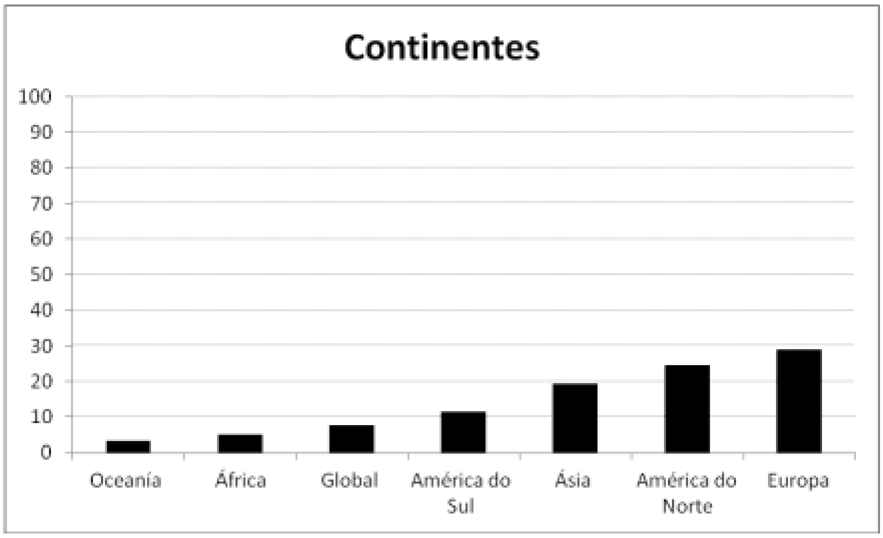

Figura 2-4: Distribuição continental das publicações. Nesta figura não foram adicionados os trabalhos de avaliação de métodos ou de revisão de metodologias, totalizando 239 artigos. As publicações que avaliaram ecossistemas em mais de um continente, foram inseridas mais de uma vez.

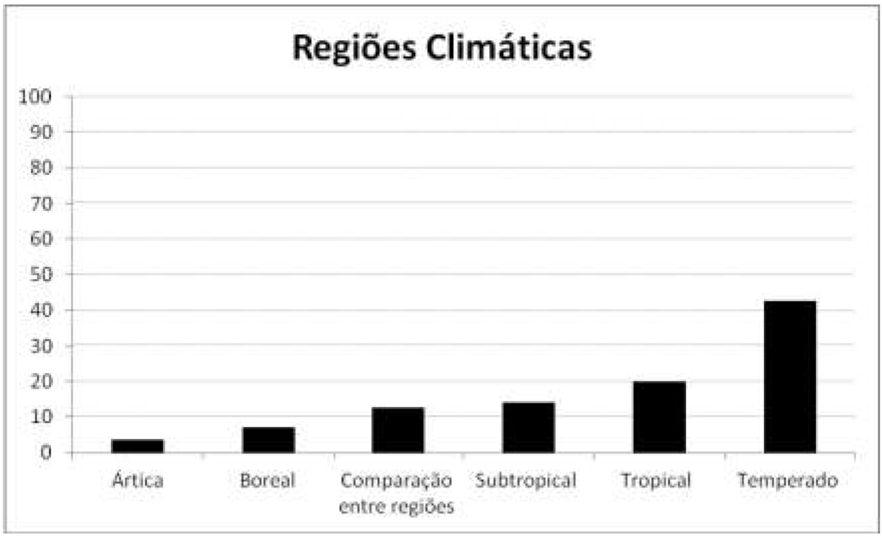

Figura 2-5: Distribuição dos trabalhos quanto as regiões climáticas. Nesta figura não foram adicionados os trabalhos de avaliação de métodos ou sem identificação da região climática, totalizando 222 artigos.

Uma significativa área da paisagem do extremo sul do Brasil é recoberta por ecossistemas aquáticos (TOMAZELLI; DILLENBURG; VILLWOCK, 2000), no entanto, o conhecimento da participação destes ecossistemas no balanço do carbono ainda é incipiente. Os estudos já realizados avaliaram as taxas de produção de CO_2 e CH_4 no sedimento de áreas alagadas de rizicultura (CANTERLE et al., 2010; CANTERLE et al., 2013). Em lagos rasos foram avaliadas as concentrações de CH_4 na coluna da água (MARINHO et al., 2009) e no sedimento (FURLANETTO et al., 2012), bem como a influência dos estandes de macrófitas aquáticas sobre as concentrações e emissões de CH_4 (MARINHO et al., 2015). Também foi estimada a emissão de CH_4, em lagos com diferentes condições tróficas em diferentes temperaturas, apontando para uma contribuição de aproximadamente 0,4 Tg ha^{-1} ano^{-1} de CH_4 via ebulição e 1,99 Tg ha^{-1} ano^{-1} via difusão (PALMA-SILVA et al., 2013). Atualmente, ainda há muitas lacunas a preencher, nas diferentes fases do balanço do carbono, principalmente no que diz respeito as taxas de produção, e a participação dos diferentes tipos de sistemas aquáticos, desde as áreas alagadas, e a interação com os sistemas lênticos e lóticos.

3 OBJETIVOS

3.1. Objetivo geral

Avaliar diferentes etapas e fatores influenciadores do balanço dos gases de carbono em ecossistemas aquáticos continentais do extremo sul do Brasil.

3.2. Objetivos Específicos

1) Estimar a influência de fatores espaciais, associados a urbanização, sobre as concentrações de CH_4 em diferentes ambientes aquáticos continentais.
2) Estimar experimentalmente a influência da temperatura nas taxas de produção de CO_2 e CH_4 no sedimento de áreas alagadas.
3) Estimar potencialmente as taxas de mineralização do carbono orgânicos em áreas alagadas, de acordo com as projeções do IPCC de elevação da temperatura.

4 ÁREA DE ESTUDO

Os ecossistemas investigados neste estudo estão localizados entre os municípios de Rio Grande e Santa Vitória do Palmar, na planície costeira do extremo sul do Brasil. A paisagem da planície costeira é reconhecida pela ampla área recoberta por ecossistemas aquáticos interconectados, incluindo o complexo lagunar Patos-Mirim-Mangueira, considerado o maior sistema lagunar do mundo (Santos et al., 2008). A paisagem da planície costeira foi formada durante o Quaternário, devido a variações no nível do mar (TOMAZELLI; DILLENBURG; VILLWOCK, 2000). O clima da região é do tipo subtropical úmido, de acordo com a classificação de Köppen (MALUF, 2000), e as temperaturas mínimas apresentam uma média de 13,4ºC no inverno, e no verão, as médias ficam em torno dos 22,6ºC (REBOITA; KRUSCHE; PICCOLI, 2006).

5 METODOLOGIA

5.1. Estimativa das concentrações na coluna da água

As concentrações de CH_4 na coluna da água foram estimadas pela metodologia proposta por Casper (1992), na qual as amostras são adicionados em frascos de borossilicato (12 ml), contendo 1,6 g (equivalente a 20% p/v) de cloreto de sódio (NaCl). Neste caso os frascos são previamente preparados com pressão negativa removendo-se o ar interno com uma seringa (60ml) e acrescentando NaCl para criar um meio supersaturado. As amostras de água (8ml) são adicionados com uma seringa (10 ml) em cada frasco, e CH_4 dissolvido na água é expelido para o *headspace* do frasco.

5.2. Estimativa das taxas de produção dos gases de carbono

Para estimar o potencial de produção do CH_4 e do CO_2 no sedimento foram coletadas amostras de áreas alagadas naturais (banhados) e artificiais (rizicultura). Os experimentos foram realizados em laboratório, onde as amostras foram acondicionadas em frascos de borossilicato (30ml), contendo uma mistura de sedimento (5g) e água (5ml), de acordo com metodologia proposta por MAROTTA et al., (2014). Os volumes de água e sedimento foram transferidos para os frascos através de uma seringa plástica (10 ml), sem a ponta, para facilitar a manipulação (DUC; CRILL; BASTVIKEN, 2010).

Os procedimentos com as amostras, antes de iniciado o experimento, estão esquematizados na Figura 5-1. Os frascos foram hermeticamente lacrados com tampas de borracha e lacres de alumínio. Após, foi criada uma condição anóxica, através do fluxo de gás nitrogênio em cada um dos frascos (BROUNS; VERHOEVEN; HEFTING, 2014; MAROTTA et al., 2014), para tanto foram fixadas agulhas nas tampas de borracha, para expelir o excesso de gás e manter o equilíbrio entre o *headspace* e a atmosfera.

As amostras foram incubadas por 90 dias em quatro câmaras reguladas em diferentes faixas de temperatura (5, 15, 25 e 35ºC). As leituras das concentrações foram realizadas em cinco tempos (0, 7, 15, 30 e 90 dias). Ao final de cada tempo, as atividades microbianas foram encerradas por acidificação, adicionando 2 ml de ácido sulfúrico (H_2SO_4, 10%) em cada frasco (MAROTTA et al., 2014). A leitura das concentrações de CO_2 e CH_4 foram realizadas com cromatógrafo gasoso Varian GC-450, em no máximo 24 horas após o término do período experimental.

Figura 5-1: Procedimentos do experimento de incubação do sedimento de estimativa das taxas de produção de gases de Carbono. 1) transferências e pesagem das amostras de sedimento (5g). 2) transferência de amostras de água (5ml). 3) lacres e tampas de borracha. 4) fechamento dos frascos. 5) Injeção de gás nitrogênio para estabelecimento da anoxía em cada frasco. 6) frascos prontos para início do experimento. 7) bandejas separadas de acordo com as faixas de temperatura e tempos amostrais acondicionadas em câmaras incubadoras, 8) frascos preparados para leitura em cromatografia gasosa (Varian® 450-GC), após cada tempo de incubação.

As taxas potenciais de produção do CH_4 e do CO_2 foram obtidas através da inclinação da reta de uma regressão linear simples, considerando a variação das concentrações dos gases estufa versos o tempo de incubação nas diferentes faixas de temperatura:

$$Y = a+b*x,$$

Onde, *b* é considerado a taxa potencial de produção anaeróbica de CH_4 e CO_2 em função do tempo experimental (90 dias), determinada em dias ($mg.g^{-1}.d^{-1}$). O tempo zero não foi considerado nesta regressão, pois o tempo de aclimatação não foi suficiente, e as concentrações foram muito mais elevadas do que nos tempos amostrais subsequentes.

5.3. Determinação das concentrações dos gases estufa

As concentrações dos gases estufa na coluna da água, sedimento e atmosfera foram determinadas no cromatógrafo gasoso (Varian® GC-450, Figura 5-1,8), provido de um detector FID para leitura do CH_4, TCD, para leitura do CO_2, usando hélio como gás de arraste. A calibragem do aparelho foi realizada com gás padrão (valores de referência: N_2O: 0,4ppm, CH_4: 2ppm, CO_2: 400ppm).

6 CAPÍTULO I - METHANE CONCENTRATIONS IN SOUTHERN BRAZIL INLAND WATERS: DEPENDENCE OF URBANIZATION, WATER QUALITY AND ECOSYSTEM SIZE

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Methane concentrations in southern Brazil inland waters: Dependence of urbanization, water quality and ecosystem size

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Abstract

Inland waters are important global compartments related to the biogeochemical processing of organic matter, and play a substantial role in methane (CH_4) budgets, which is the main end product of organic carbon anaerobic decomposition and an important greenhouse gas (GHG). The interrelationships among biological, physical and chemical variables regulate CH_4 concentrations in inland waters. The environmental and inherent ecosystems characteristics, including nutrient loads, trophic condition, and carbon budget may be affected by urbanization. In this study, we analyzed water column characteristics, including trophic status and CH_4 concentrations in urban and non-urban inland waters. The means of CH_4 concentrations varied among 0.675±0.597 $\mu mol.L^{-1}$ and 9.086±4.346 $\mu mol.L^{-1}$, with significant differences ($p<0.001$) among urban and non-urban ecosystems. Urban ecosystems showed higher nutrient and CH_4 concentrations, which showed a positive correlation ($p<0.05$) with trophic status. Beyond these factors, ecosystem size showed effects on the CH_4 concentrations in the water column. Once lower concentrations were found in larger ecosystems, even when located inside urban limits. The conservation of the natural condition, and characteristics of larger inland waters are thus essential to mitigate the eutrophication and CH_4 imbalance that is due to urbanization effects.

Key words: inland waters, organic carbon, landscape use, greenhouse gas, eutrophication.

Introduction

Inland waters play a substantial role in the global biogeochemical processing of organic matter (Downing 2010). These ecosystems are among the most important natural carbon compartments, acting as sinkers and transporters of carbon (Cole et al. 2007), and a source of methane (CH_4), the second most important greenhouse gas (GHG) (Saunois et al. 2016). Inland waters thus participate in climate regulation beyond their effect on carbon budget (Tranvik et al. 2009). This contribution to the global process is associated with the significant area that these ecosystems occupy in the landscape, and their capacity to process organic material (Downing et al. 2006).

Methane is the end product of organic carbon decomposition, which is produced under anoxic conditions (Bastviken et al. 2004; Saunois et al. 2016). CH_4 production, consumption and emission are steps of the carbon budget in aquatic ecosystems, and determine the concentrations in the water column and sediment, as well as the exchange acorss the sediment-water (Natchimuthu et al. 2014). The difference between CH_4 production and oxidation determines the concentrations in the sediment (Saunois et al. 2016), and water column, as well as the fluxes through the water column, and how much CH_4 can be diffused to the atmosphere (Natchimuthu et al. 2014; Saunois et al. 2016), and the effect on the climate process (Kaushal et al. 2014).

The CH_4 metabolism are strongly affected by temporal and spatial factors, such as oxygen concentrations, nutrient availability, pH, temperature (Bastviken et al. 2004; Cole et al. 2007; Marinho et al. 2009; Palma-Silva et al. 2013) and food web (Schilder et al. 2017). The autochthonous production (Marinho et al. 2015; Schilder et al. 2017) and allochthonous inputs of nutrients carried from terrestrial landscape (Cole et al. 2007; Furlanetto et al. 2012; Yang et al. 2016; Saunois et al. 2016), are other essential factors that may affect CH_4 metabolism, and elevate nutrient concentrations in the sediment (Furlanetto et al. 2012). Beyond CH_4 production and emission (Marinho et al. 2009; Crawford et al. 2017), these factors may all change the properties of the aquatic ecosystem, which are directly related to CH_4 budgets (Bastviken et al. 2004; Downing 2010; Kaushal et al. 2014).

Aquatic ecosystems are affected by the expansion of urban areas, which promotes changes in the natural characteristics of the landscape and characteristics of water bodies, through water withdrawal, the discharge of sewage water, and storm water runoff (Yang et al. 2016). The input of organic matter and nutrients may promote losses in water quality, and unbalance carbon (Tranvik et al. 2009; Kaushal et al. 2014), and CH_4 concentrations in the water column (Marinho et al. 2009). The urbanization process is thus associated with a rise in nutrient loads, and may amplify CH_4 production, concentrations and emission (Kaushal et al. 2014; Saunois et al. 2016).

Studies related to landscape use contribute to a better understanding of how nutrients and carbon is processed in agricultural and urban watersheds (Kaushal et al. 2014). In southern Brazil, despite the wide area covered by inland waters, little is known about urban influences on theses ecosystems. Studies related to the CH_4 budget are predominantly related to temporal scales, such as seasonal variations in water-column concentrations (Marinho et al. 2009), as well as diffusion and emission (Palma-Silva et al. 2013). The studies related to spatial scale were undertaken in different compartments of the same ecosystem (Palma-Silva et al. 2013; Marinho et al. 2015) or in nearby ecosystems (Marinho et al. 2009; Furlanetto et al. 2012). For example, is know that weather conditions promote annual variations of temperature around 10°C, which is sufficient to significantly alter CH_4 concentrations in the water column (Marinho et al. 2009), and CH_4 emissions (Palma-Silva el al. 2013; Marinho et al. 2015). Allochthonous input contributes to determining the trophic status and elevates the concentration of CH_4 in sediment of shallow lakes (Furlanetto et al. 2012).

We estimate the water column CH_4 concentrations in aquatic ecosystems located near urban and non-urban areas. The aims of this study were: i: evaluate the spatial factors and environmental variables that influence CH_4 concentrations in urban and non-urban inland waters; and ii: better understand how the changes in the landscape associated with urbanization can affect CH_4 concentrations in inland water ecosystems.

Material and Methods

Study area

We studied aquatic ecosystems located in the southern Brazilian coastal plain. This landscape was formed during the Quaternary period by successive sea level fluctuations (Tomazelli et al. 2000). The regional weather conditions are humid subtropical, according to classification by Köppen (Maluf 2000). The means of annual temperature vary between 13ºC (winter) and 24ºC (summer), with annual rainfall varying between 1200 and 1500 mm (Palma-Silva et al. 2013). The landscape is occupied by different aquatic ecosystems, and composed of a series of interconnected wetlands (Maltchik et al. 2004; Rolon et al. 2010; Schreiner et al. 2015), small shallow lakes (Marinho et al. 2009, 2015, Palma-Silva et al. 2013), ponds, large freshwater lagoons, and sandy streams (Tomazelli et al. 2000).

To includes a representative range of environmental conditions and factors we sampled lentic and lotic inland waters that varied in area, trophic state, and localization (urban and non-urban) within the municipality of Rio Grande (32°07' 06.2" S; 52°20' 37.2"W). According to the Brazilian Institute of Geography and Statistics (IBGE), the city covers an area of 2,709.522 km^2 with an estimated population greater than 200,000 inhabitants, of which fewer than 8,000 inhabitants live in a non-urban area (https://cidades.ibge.gov.br/brasil/rs/rio-grande/panorama).

The ecosystems located in the urbanized (U1 to U5) region (n=5), are surrounded by buildings, streets, civic squares, fields, trees, and various anthropic activities. The Bolaxa Stream (U1) has a trophic status that varies from oligotrophic to mesotrophic, with approximately 4 km of extension, is surrounded by zones with riparian forest, habitations and farming, and the waters flow from a wetlands system to Verde Lagoon (Telöken et al. 2014). The Verde Lagoon (U2), is mesotrophic, has an area of approximately 16 km^2, which is surrounded by wetlands and streams, and is located in an area of Municipality Environmental Protection. The Biguás lake (U3) and the Polegar Lake (U4) are located inside a university campus (Palma-Silva et al. 2013). The former has a trophic status that varies between mesotrophic and eutrophic, an area of approximately 0.015km^2, and U4 that varies between oligotrophic and mesotrophic, with an area of approximately 0.01km^2 (Marinho et al. 2015). The Tamandaré Lake (U5) is a eutrophic artificial pond, with an area of approximately 0.01km^2, located inside a central civic square in Rio Grande city.

The ecosystems in the non-urbanized (NU1 to NU5) region (n=5) are located near Taim Ecological Station, surrounded by wetlands, dunes, forests, fields, grasslands cultures, and agriculture crops. The largest lagoons are influenced by small urbanized areas in some parts. The São Gonçalo Channel (NU1), has a trophic status that varies between mesoeutrophic and eutrophic, with 70km of extension that links with the Patos-Mirim lagoon system (Albertoni et al. 2017). The Mirim Lagoon (NU2), is mesotrophic, and has an area of approximately 3920 km^2. The Mangueira Lagoon (NU3), varies in trophic status from mesotrophic to oligotrophic, with an area of approximately 820 km^2 (Santos et al. 2008; Fragoso Jr. et al. 2011). The Caiubá Lagoon (NU4) has a trophic status which varies between mesotrophic to eutrophic, with an area of approximately 30 km^2, and is an important resource for rice cultivation (Cunha et al. 2013). The Flores Lagoon (NU5), is mesotrophic, with an area of approximately 9.7 km$^{2.}$

Sampling and analysis

We collected the field samples throughout 2012, taking seasonal measurements (n=4; January, May, August, and November), and five samples (n=5) in each ecosystem. We subsequently aggregated ecosystem mean values amounting to 20 samples for each ecosystem. Measurements in the field were made directly in the surface water pH, and dissolved oxygen (DO) with a calibrated probe (Horiba U-50$^{®}$). The water samples for the physicochemical variables in all ecosystems were collected between 9:00h and 15:00h, in approximately 1m depth, in unvegetated littoral margins. We stored water samples in dark bottles after collection. To determine the CH_4 concentrations, we took water samples with a syringe (8ml) and injected them into a sealed 12ml glass flask with negative pressure, containing 1.6g of NaCl.

In the laboratory we determined the following variables: chlorophyll-*a* (chl-*a*; Chorus and Bartram 1999), total phosphorus (TP; Valderrama 1981), total nitrogen

(TN; Mackereth et al. 1978), and nitrate (NO_3) using an ionic chromatograph (Dionex®). Suspended material was measured using the gravimetric method, before water samples were filtrated (GF/C Whatman®, USA) and dried (60°C). The total organic carbon (TOC) was determined using a TOC-VCPH (Shimadzu®), and before estimating TOC, the water samples were acidified with nitric acid ($pH<2.0$). The CH_4 concentrations were measured using a gas chromatograph (Varian® 450; GC) with a flame ionization detector (FID). The gas chromatograph was calibrated using certified standard gas (CH_4: 2 ppm).

We used chl-*a* and TP concentrations to determine the trophic state index (TSI) of the inland waters, according to methodology proposed by Cunha et al. (2013), for tropical and subtropical reservoirs. We used polygon creation to estimate the area (km^2) of the ecosystems studied with Google Earth Pro® software.

Analysis of data

We analyzed the differences between CH_4 concentrations in the water columns of the ten ecosystems using one-way analysis of variance (ANOVA) with Tukey's post-test for multiple comparison. We used the Student's *t*-test to analyze the differences between the physical and chemical variables of urban and non-urban aquatic ecosystems, and Spearman's (*rs*) coefficient to test correlation between CH_4 and environmental variables. We selected the variables with significant correlations (*rs*; $p<0.05$) to begin the principal component analyses (PCA), and grouped inland waters ecosystems, using the correlation matrix in the PCA. We used the PCA scores (PC_1 and PC_2) from each aquatic ecosystem to estimate the effect of environmental factors on the CH_4 concentration, through a simple linear regression. We used the CH_4 concentrations as the dependent variable, and PC_1 and PC_2 as the independent variables. We also used linear regression to analyze the relationship between CH_4 and localization (urban and non-urban) and ecosystem area (km^2). U1 and NU1 were not included in liner regression as they are lotic ecosystems.

Before undertaking statistical tests, we checked the CH_4 concentration data for normality (Kolmogorov-Smirnov test), homogeneity of variance (Bartlett's test) and linearity. We transformed CH_4 concentrations (Log_{10}) to minimize the variance, linearize the responses and normalize the distribution. All statistical analyses and graphs were performed with R Software R-3.2.2 (R Core Team 2016).

Results

Methane concentrations

The means of CH_4 concentrations ranged from 0.675±0.597 $\mu mol.L^{-1}$ to 9.086±4.346 $\mu mol.L^{-1}$, with significant differences ($p<0.001$) between urban and non-urban ecosystems (Fig. 6-1). The highest mean concentration was observed in the lotic urban (U1) ecosystems. Only one of the urban ecosystems (U2), showed significant differences in relation to the other ecosystems located in urban areas (Fig. 1, $p<0.001$).

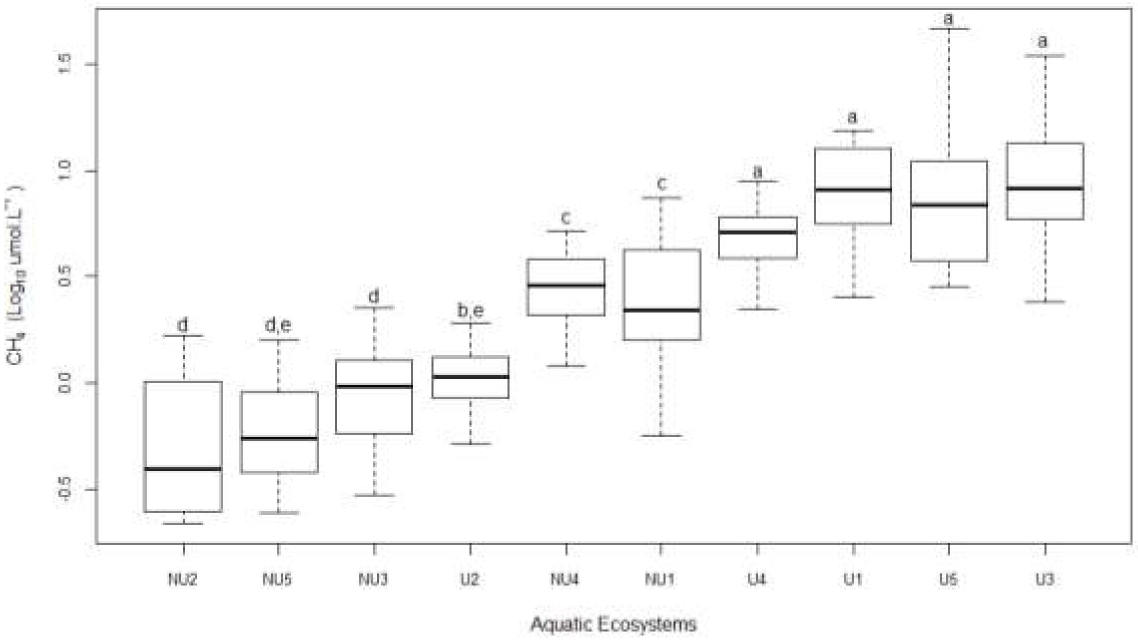

Fig. 6-1 Comparison between methane concentration (µmol.L^{-1}) in the ten aquatic ecosystem (n=20). The graphic was ordered according to CH_4 concentration in the water column. The y axis is logarithmic. Significant differences of at least $p < 0.05$ are indicated by different letters

Environmental variables and relationship to CH_4 concentrations

The means of the environmental variables are shown in Table 6-1; the values were predominantly higher in urban ecosystems, although without significant differences ($p>0.05$) between urban and non-urban ecosystems. However, there are important factors highlight differences between ecosystems. First, trophic status varied in non-urban ecosystems between ultraoligotrophic (NU3) and mesotrophic (NU1), with oligotrophic (NU2, NU4, NU5) the prevailing condition. Second, the trophic status in urban ecosystems varied from oligotrophic (U4) to eutrophic (U5), with a prevalence of mesotrophic (U1, U2, U3) conditions (Table 1). Third, U5, which is located inside a central civic square, showed higher means of chl-*a*, NO_3, TN, and TP. The correlation between environmental variables and CH_4 concentrations (Table 6-2) shows that chl-*a* and TP concentrations, which are related to trophic status index (TSI), showed

Table 6-1: Mean(n=20) ± standard deviations (SD) of water column variables: dissolved oxygen (DO), pH, electrical conductivity (EC), suspended material (SM), chlorophyll-*a* (chl-*a*), nitrate (NO$_3$), total phosphorous (TP), total nitrogen (TN), total organic carbon (TOC), trophic status index (TSI). Trophic state categories (ULO - ultraoligotrophic, OLG- oligotrophic, MES - mesotrophic, EUT - eutrophic), and the p value of the Student's *t*-test of the differences between urban and non-urban inland waters. Significant p values are in bold

Ecosystem	**Size**	DO (mg.L^{-1})		pH		EC (μS)		SM (mg.L^{-1})		chl-*a* (μg.L^{-1})		NO$_3$ (μg.L^{-1})		TP (mg.L^{-1})		TN (mg.L^{-1})		TOC (mg.L^{-1})	
		mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
U1	[a] 4 Km	5.01	5.56	8.57	2.41	827.50	638.70	12.60	6.59	13.12	10.00	11.98	6.72	0.07	0.04	0.94	1.08	21.27	3.96
U2	16 Km^2	10.17	2.59	8.09	0.78	205.90	268.81	59.75	29.16	23.13	14.08	6.96	9.26	0.06	0.02	0.58	0.63	9.16	3.22
U3	0.015 Km^2	7.93	1.53	8.40	1.34	253.00	59.34	13.99	15.53	17.96	7.25	26.88	24.76	0.05	0.04	0.52	0.51	8.21	1.79
U4	0.010 Km^2	9.07	2.29	7.99	1.62	113.75	51.59	7.46	7.72	7.45	1.89	4.28	5.29	0.03	0.01	0.90	0.93	7.10	1.74
U5	0.010 Km^2	8.04	1.08	7.86	0.46	362.17	150.61	30.07	25.30	60.61	6.20	23.06	0.80	0.10	0.00	1.39	0.13	6.68	1.36
Mean		8.04	3.23	8.18	1.4	352.46	379.60	24.77	25.27	24.54	25.33	14.63	18.24	0.06	0.03	0.86	0.87	10.48	6.07
NU1	[a] 70 Km	10.15	2.34	7.30	0.36	122.50	16.58	70.50	66.29	13.90	6.85	2.57	3.67	0.06	0.02	0.42	0.34	5.51	1.01
NU2	3920 Km^2	9.82	1.08	7.74	0.28	121.50	13.40	56.13	20.42	17.85	21.05	2.50	3.24	0.04	0.01	0.42	0.37	5.29	1.32
NU3	820 Km^2	10.04	2.23	7.54	0.36	446.33	95.13	4.85	0.72	4.32	1.83	0.98	1.47	0.03	0.01	0.44	0.39	6.52	1.16
NU4	30 Km^2	7.68	3.06	6.75	0.83	144.50	63.98	55.98	44.93	5.87	1.73	2.54	1.21	0.03	0.02	0.71	0.71	8.48	2.32
NU5	9.7 Km^2	9.51	1.75	6.99	0.32	181.67	23.47	23.80	10.29	6.59	1.85	1.32	1.47	0.03	0.02	0.55	0.46	6.01	0.70
Mean		9.44	2.16	7.26	0.56	203.30	135.20	42.25	41.35	9.71	10.39	1.98	2.28	0.04	0.02	0.51	0.44	6.36	1.71
p		**0.05**		**0.41**		**0.41**		**0.90**		**0.29**		**0.12**		**0.34**		**0.30**		**0.34**	

[a] Indicate a lotic ecosystems and the ecosystem distance in Kilometres

significant correlations ($p<0.05$) with CH_4 concentrations, as well as NO_3 ($p<0.005$) and TOC ($p<0.05$) concentrations.

Table 6-2: Spearman's (*rs*) correlation between the concentrations of CH_4 and physicochemical variables considering the correlation of the ten inland waters (n=40). dissolved oxygen (DO), pH, electrical conductivity (EC), suspended material (SM), chlorophyll-*a* (chl-*a*), nitrate (NO_3), total phosphorous (TP), total nitrogen (TN), total organic carbon (TOC), and trophic status index (TSI)

	CH_4	
	rs	*p*
DO	-0.260	0.090
pH	0.038	0.815
EC	0.195	0.228
SM	-0.208	0.198
chl-*a*	0.321	0.040*
NO_3	0.435	0.005*
TP	0.315	0.040*
TN	0.082	0.617
TOC	0.327	0.040*
TSI	0.343	0.030*
* $p < 0.05$		

In the PCA, the first (72.76%) and second (20.82%) components explained 93.58% of the total data variation (Fig. 6-2). The higher load of the first component (PC_1) corresponded to higher values of chl-*a*, TSI, and TP, and were mainly found in U5, the eutrophic urban ecosystem. The second component (PC_2) showed a higher load related to TOC, both urban and no-urban ecosystems are distant to urban stream, which showed higher TOC concentrations. Non-urban ecosystems showed lower distances between environments, and the distribution of urban ecosystems were wider.

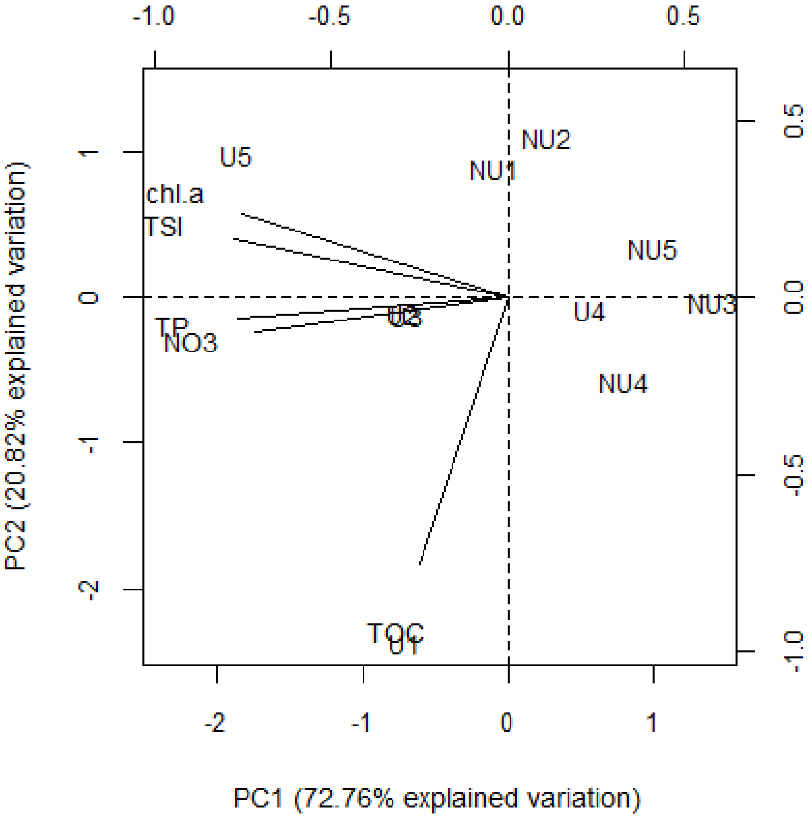

Fig. 6-2 Results of PCA of the physicochemical variables from the ten ecosystems. PC_1 explains 72.76% of the variation and PC_2 explains 20.82% of the variation. Abbreviations: total phosphorous (TP), nitrate (NO_3), total organic carbon (TOC), and trophic status index (TSI), chlorophyll-a (chl-a)

The linear regression relating CH_4 concentrations to environmental factors (Fig. 6-3) shows some important factors highlighting the differences between ecosystems. First, CH_4 concentration increased exponentially associated with trophic status and NO_3 concentration (Fig. 6-3a, p=0.023). Second, despite the lack of a statistically significant relationship (Fig. 6-3b, p=0.379) it´s possible to see that TOC concentrations affect the CH_4 concentrations. The non-urban ecosystems had lower TOC, ranging from 8.48±2.32 mgL^{-1} to 5.29±1.32 mgL^{-1}, and U2, which was greater than other urban ecosystems, showed similar characteristics in relation to non-urban ecosystems.

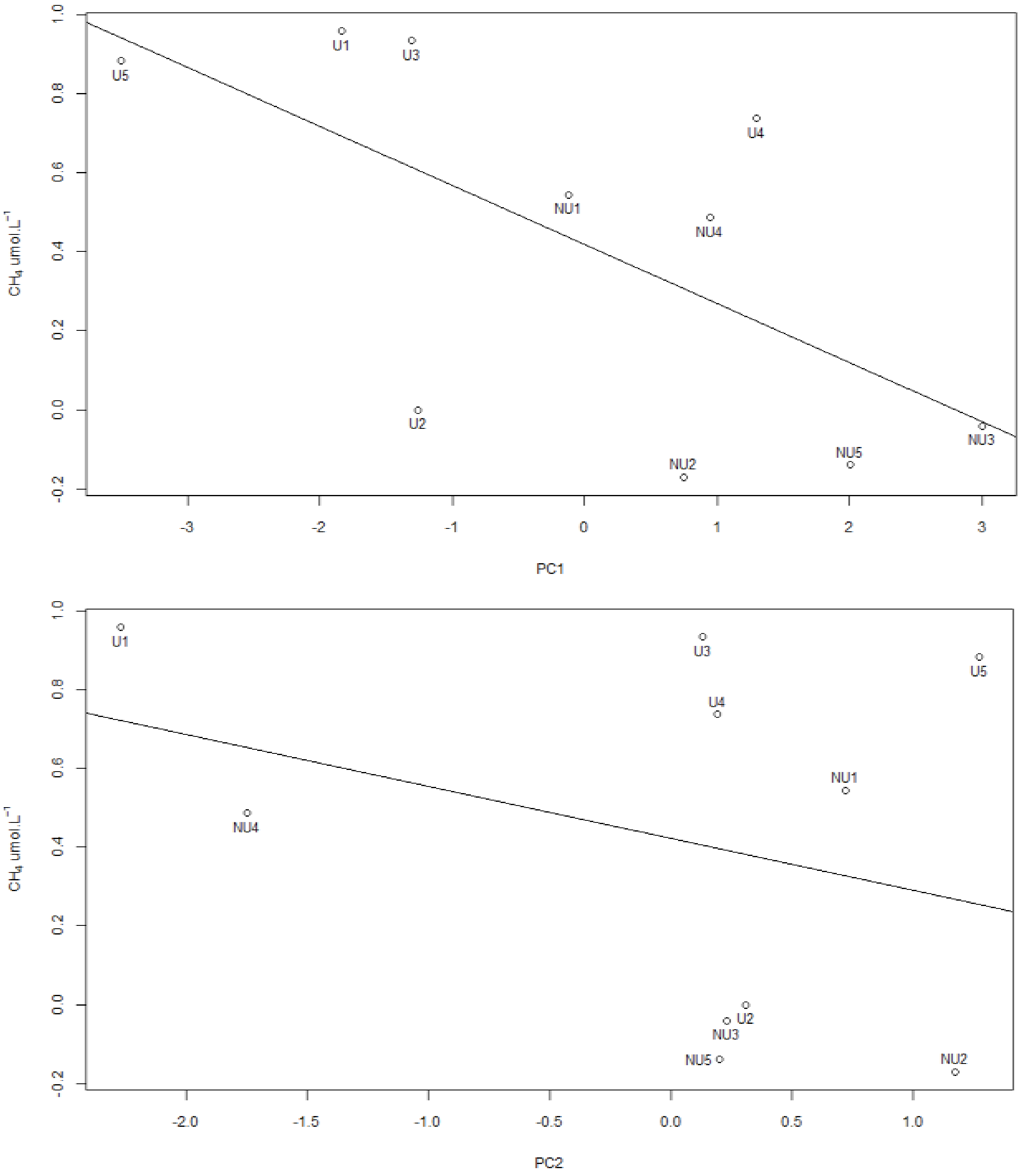

Fig. 6-3 Relationship between CH$_4$ concentrations (µmol. L^{-1}) with PCA components (a) PC$_1$, corresponds to variables related to eutrophic condition and (b) PC$_2$, corresponds to carbon concentration in the water column. The solid line shows the linear regression. The R^2 value was 0.627 ($p<0.05$) and 0.22 ($p>0.05$) for PC$_1$ and PC$_2$, respectively. All studied ecosystems are represented and the solid line represents the linear regression

Relationship between CH_4 concentrations and inland water size

The size of the lentic ecosystems were highly varied (Table 1). There was a significant relationship between CH_4 concentrations and ecosystem size (Fig. 6-4, $p=0.013$). Non-urban ecosystems are predominantly larger than urban ecosystems, and showed lower CH_4, TOC, nutrients (TN, NO_3 and TP) and chlorophyll-*a* concentrations. The largest urban ecosystems (U2) showed significantly lower ($p<0.05$) concentrations in relation to other urban ecosystems, and the biggest inland water (NU2) returned the lowest mean for CH_4 concentrations.

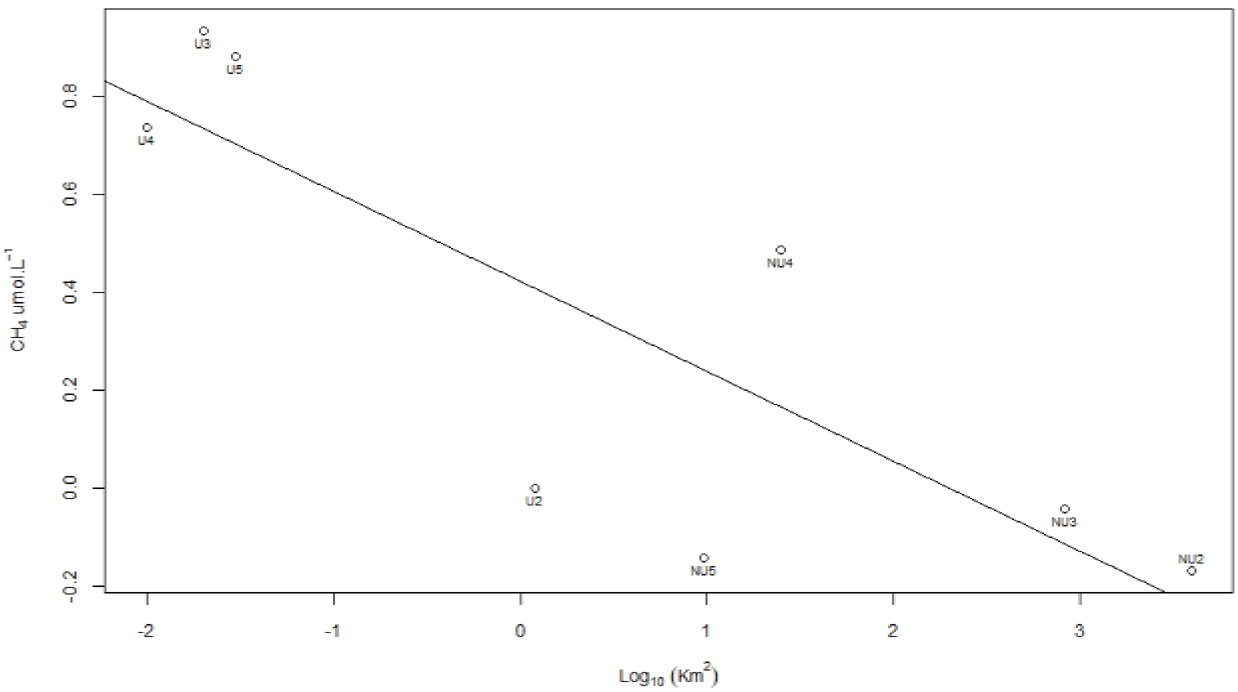

Fig. 6-4 Relationship between CH_4 concentration (μmol. L^{-1}) and lake surface area (km^2) of the lentic ecosystems (n=8). The solid line shows the linear regression. The R^2 value was 0.690 ($p<0.05$)

Discussion

The means of CH_4 concentrations in the water column surface observed in our study (0.68 μmol.L^{-1} to 9.09 μmol.L^{-1}) were relatively higher than concentrations found in environments located in other climatic regions, and there is similar variation when compared with lakes located in the same landscape. In an estimation of CH_4 emissions from North American and Swedish lakes, Bastviken et al. (2004) reported concentrations in the water column within 0.27 to 2.32 $\mu mol.L^{-1}$ and 0.08 to 1.89 $\mu mol.L^{-1}$, respectively. In a hypertrophic lake, in the Netherlands, Schilder et al. (2017) found very high concentrations in the bottom of the water column (479 $\mu mol.L^{-1}$) in relation to the surface of the water column (1.1 $\mu mol.L^{-1}$). In Southern Brazilian study of two of the urban lakes also investigated here, Marinho et al. (2009) observed CH_4 concentrations of 0.41 to 3.66 $\mu mol.L^{-1}$ (U3) and 1.19 to 1.43 $\mu mol.L^{-1}$ (U2). Palma-Silva et al. (2013), observed concentrations between 0.27 $\mu mol.L^{-1}$ (winter) and 2.49 $\mu mol.L^{-1}$ (summer) in U4, when in a mesoeutrophic condition, and between 0.95 $\mu mol.L^{-1}$ (winter) and 19.92 $\mu mol.L^{-1}$ (summer), in U3 when in a eutrophic condition. The average concentrations (0.03 $\mu mol.L^{-1}$) found by Santos et al. (2008) in a non-urban lagoon (NU3) were lower than the lowest mean found in the present study. The differences found, mainly in the same ecosystems may be related to variation in the period of sampling, input of nutrients, and trophic conditions.

The higher CH_4 concentrations in urban ecosystems showed lower variation, which was related to higher nutrient concentrations and trophic status. These ecosystems presented a range of trophic states, from oligotrophic to eutrophic, whereas non-urban ecosystems varied between ultraoligotrophic and mesotrophic. Urban expansion should change the contribution of aquatic ecosystems in relation to carbon budgets (Tranvik et al. 2009; Huang et al. 2017). According to Kaushal et al. (2014) urbanization amplifies nutrient loads in inland waters, and also amplifies phosphorus, nitrogen and carbon exports from watersheds. In non-urban ecosystems, the inputs of rice irrigation channels may represent an important source of groundwater and nutrients

(Santos et al. 2008). The high nutrient concentrations promote eutrophication, which may encourage the depletion of oxygen concentrations (Downing 2010), a favorable condition for CH_4 production in anoxic compartments, and consequent elevations in CH_4 concentrations in the surface and bottom water column (Marinho 2009; Clayer et al. 2016; Schilder et al. 2017).

The ecosystems with low nutrient concentrations and well oxygenated water columns demonstrated favorable conditions for oxidized CH_4 in the water column, sinking the CH_4 in the sediment or emitting it directly to the anoxic sediments (Bastviken et al. 2004; Clayer et al. 2016). CH_4 concentration in the surface water column is a function of CH_4 produced in anoxic compartments and oxidation, which determines the CH_4 concentrations and fluxes (Bastviken et al. 2004; Clayer et al. 2016). When the environmental conditions are favorable, the CH_4 produced in anoxic sediments can be transferred to the water column through diffusion or ebullition (Natchimuthu et al. 2014) and eventually may be emitted to the atmosphere (Palma-Silva et al. 2013; Clayer et al. 2016). The low oxygen concentrations are more favorable for CH_4 release to the sediment than environments perennially exposed to oxygen (Clayer et al. 2016). In our study, higher CH_4 concentration in urban environments was negatively correlated with dissolved oxygen concentrations The negative correlation between oxygen concentrations and CH_4 may indicate a favorable condition to CH_4 release and exchange among sediment-water-atmosphere.

The U1 is an urban stream that showed lower dissolved oxygen concentrations, associated with the highest CH_4 and TOC concentrations. Streams contribute to carbon fluxes, and are significant CH_4 sources to the atmosphere, with the spatial capacity to produce and lose CH_4 (Stanley et al. 2016). In our study, the U1 stream shores were surrounded by small urbanized areas, riparian native trees, and wetlands, which were well colonized by aquatic macrophyte stands (Telöken et al. 2014), which can contribute to higher carbon concentrations and low dissolved oxygen concentrations (Marinho et al. 2015). The urbanization process (Kaushal et al. 2014), the allochthonous input (Marinho et al. 2009; Furlanetto et al. 2012; Stanley et al. 2016; Crawford et al. 2017), and presence of riparian wetlands (Yang et al. 2016) are important sources of dissolved organic material. Autochthonous and allochthonous organic matter are essential sources of carbon accumulation (Huang et al. 2017). Lotic ecosystems that drain higher organic soils may have higher dissolved organic and inorganic carbon concentrations (Abril et al. 2015). All these factors directly affect the aquatic metabolism, which includes CH_4 concentration in the sediment (Furlanetto et al. 2012), the water column (Marinho et al. 2009), and an elevated CH_4 emission (Palma-Silva et al. 2013).

We observed that smaller environments showed higher methane concentrations. For example, U2, the largest urban ecosystem, showed CH_4 concentrations that were statistically lower in relation to other urban environments, and similar values in relation to non-urban ecosystems. Aquatic ecosystem size proved to be an important factor associated with the differences between CH_4 concentrations. Larger ecosystems generally showed lower capacity for processing organic carbon than smaller lakes and ponds (Downing et al. 2006). Small lakes and ponds are generally ignored in relation to their global participation in carbon processing, however, the rates and quantities of buried and processing carbon are more intense and dynamic than in larger water bodies (Downing 2010), as are the concentrations and emissions of CH_4 (Bastviken et al. 2004). Natural small water bodies are predominantly systems that act as depressional wetlands, and therefore constitute effective carbon traps in the landscape (Premke et al. 2016). Using the concentrations and gas exchange from 472 lakes and ponds smaller than 674 km^2 to estimate the CO_2 and/or CH_4 fluxes, Holgerson and Raymond (2016) showed that small ponds represent an important source in the global carbon budget.

The development of studies related to understanding the interrelationship of environmental factors in urban areas contributes to understand the human-environment systems (Ngo and Pataki 2008). Our results indicate that rise in the CH_4 concentrations is related to high nutrient concentrations, eutrophic status, localization in urban areas, and ecosystem size. Smaller inland waters ecosystems are predominantly distributed in urbanized areas, and showed higher CH_4 concentrations. The expansion of urban areas promotes changes in the water body characteristics (Yang et al. 2016), including CH_4 concentrations (Kaushal et al. 2014). This reinforces the importance of conserving the natural characteristics of the landscape. The urbanization process may promote changes in water quality and CH_4 concentrations. Maintaining the natural characteristics of the areas surrounding aquatic ecosystems is essential for mitigating the input of material and autochthonous production, and preventing the potentially higher emission of GHG. Although we have reported on the effects of urbanization and ecosystem sizes, more studies should be undertaken, including a larger number of inland waters, of different sizes, to improve this knowledge, and demonstrate that a reduction in the area and alteration in the characteristics of natural areas affect the CH_4 budget.

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7 CAPÍTULO II - POTENTIAL CARBON GAS PRODUCTION IN SOUTHERN BRAZIL WETLAND SEDIMENTS: POSSIBLE IMPLICATIONS OF AGRICULTURAL LAND USE AND WARMING

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Potential carbon gas production in southern Brazil wetland sediments: possible implications of agricultural land use and warming

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Abstract

Methane (CH_4) and carbon dioxide (CO_2) are greenhouse gases (GHG) important in the carbon cycle that exchanges carbon between ecosystems and the atmosphere. To determine how rice paddy fields and temperature affect the carbon budget, we experimentally estimated CH_4 and CO_2 concentrations and production in sediments from natural and rice wetlands over a temperature gradient. Moreover, we estimated how much GHG production rates would increase in these ecosystems, according to the IPCC projections for temperature rise caused by global warming. Our results showed that the concentrations and potential production rates of GHG showed no significant differences between natural and rice wetlands, although the accumulation of organic matter and nutrients was higher in natural wetland sediments. However, temperature elevation played a significant role in the rise of gas production rates. According to our results, projected increased atmospheric temperature may promote increases in the rates of production and concentrations of carbon gases. The potential carbon gases production in the scenario of atmospheric warming indicated that CH_4 (18.91%) may be higher than CO_2 (4.54%), mainly in rice wetlands. This reinforces the importance of natural wetland conservation.

Keywords: Carbon cycle; climate change; sediment; agriculture; subtropical coastal plain.

Introduction

Wetlands are among the most important ecosystems worldwide with regard to their distribution, socio-economic, and ecological importance (Ramsar Convention Bureau 2001). The potential distribution of global inland wetlands is approximately 29.83 million km^2, but the extent of the remaining areas could range from1.53 to 14.86 million km^2 (Hu et al. 2017). Due to their wide distribution, wetlands provide important services, including water supply, microclimate regulation (Junk et al. 2014), carbon sequestration and storage (Cao et al. 1996, Mitra et al. 2005, Mitsch et al. 2013), and GHG budgets (Bridgham et al. 2006, Inglett et al 2012). These services are recognized as being anthropogenically useful (Mitsch and Gosselink, 2000) and thus receive value if well conserved (Junk et al. 2014). For example, when agriculture replaces natural wetlands (Bridgham et al. 2006, IPCC 2007, Rolon et al. 2010, Junk et al. 2014), it can promote losses in the natural landscape, changes in key ecosystem services, and increases in carbon loading, and these may play an important role in GHG and temperature variations (Kaushal et al. 2014; Meijide et al. 2017).

Both CH_4 and CO_2 are important in the carbon cycle and involve continuous gas exchange between ecosystems and the atmosphere (IPCC 2007). In wetlands, sediment, aquatic vegetation (photosynthesis), and heterotrophic respiration (including anaerobic decomposition of organic detritus) promote the circulation and return of carbon to the atmosphere as CH_4 or CO_2 (IPCC 2007, Stern et al. 2007, Kayranli et al. 2010). Wetland sediments are therefore an important carbon compartment associated with accumulation, storage, and transformation (Segers 1998, Cole et al. 2007, Keller et al. 2009). The anaerobic carbon mineralization process prevails in the sediment due to low oxygen penetration, which is an important condition for the carbon transformation process (Cunha-Santino and Bianchini 2013). Within anaerobic sediments, methanogenesis (process of CH_4 production) is the last step of organic carbon mineralization, and it takes place in reduced sediment conditions (Cao et al. 1996, Smith et al. 2003, Kayranli et al. 2010). Moreover, changes in nutrient availability may promote increase in the activity of methanogens that can significantly affect carbon cycling in wetland sediments (Kim et al. 2015). These transformations, depending on meteorological and hydrological conditions, determine whether wetland sediments are sinks or sources of CH_4 and CO_2 to the atmosphere (Kayranli et al. 2010) and to climate feedback (Marotta et al. 2014).

The aquatic macrophyte community is another important regulating factor associated with the production and emission of CH_4 and CO_2 gases (Sutton-Grier and Megonigal 2011, Petruzzellla et al. 2013). They play an important role in production rates of CH_4 through their detritus (Inglett et al. 2012, Marinho et al. 2015), influencing the amount of easily degradable carbon (Segers 1998, Bodker et al. 2015) that can raise gas concentrations in the sediment (Furlanetto et al. 2012). Moreover, aquatic macrophyte traits such as biomass induce changes in the electron acceptor abundance, which can lead to competition for carbon among microbes (Sutton-Grier and Megonigal 2011), and suppressing the methanogenesis (Bodelier 2011).

The presence of emergent aquatic macrophytes can be favorable to gas emissions from the sediment, depending on the production and oxidation rates in the sediment (Bastviken et al. 2004, Marinho et al. 2015). Moreover, in natural freshwater wetlands, greater aboveground plant biomass promotes accumulation of carbon and litter with high organic matter quality and decomposition rates (Bodker et al. 2015), while the decomposition of rice crop detritus may release large amounts of carbon, which the concentrations decline rapidly (Villegas-Pangga et al. 2000).

Organic carbon mineralization rates in inland waters are highly temperature dependent (Schulz and Conrad 1996, Segers 1998, Inglett et al. 2012, Cunha-Santino and Bianchini 2013, Marotta et al. 2014). Higher temperatures elevate CH_4 and CO_2 production in wetlands (Segers 1998, Kayranli et al. 2010, Inglett et al. 2012). Greater production of CH_4 and CO_2 is related to warmer temperatures and nutrient-concentrated sites, which are associated with wetlands dominated by aquatic macrophytes (Inglett et al. 2012). In rice paddy fields, the application of fertilizer should lead to the elevation of anaerobic decomposition of organic material and a consequent increase in CH_4 production (Canterle et al. 2013, Meijide et al. 2017).

In southern Brazil coastal plains, a significant portion of the landscape is covered by natural and rice wetlands (Maltchik et al. 2004, Schreiner et al. 2015). The expansion of rice production is a threat to natural wetlands, since more than 90% of natural systems have already been lost and the remaining ones are still at high risk due to expansion of rice production (Rolon et al. 2010). Studies of temporal rice wetlands in the region have suggested that differences between organic matter and carbon in the sediment could result in temporal variations of CH_4 and CO_2 production rates (Canterle et al. 2013). The effects of agricultural land use on organic carbon mineralization and consequent GHG production associated with warming in subtropical south Brazil wetlands remain unknown.

To better understand the CH_4 and CO_2 budgets in this region, we experimentally estimated temperature effects on the anaerobic rates of organic carbon mineralization in natural and rice wetland sediments over a temperature gradient, considering the important role of aquatic macrophyte detritus in the production of carbon gases and the presence of dense stands in natural wetlands. We hypothesize that (1) the concentrations and production rates of CH_4 and CO_2 in the sediment will be higher in natural wetlands compared to rice wetlands, and (2) warming will increase organic carbon mineralization and the production rates of CH_4 and CO_2.

Materials and methods

Study area

Sediment samples were taken from natural and rice wetlands between the municipalities of Rio Grande (32°07'06.2"S; 52°20'37.2"W) and Santa Vitoria do Palmar (33°17'02.0"S; 53°03'45.5"W), in southern Brazil coastal plains (Fig. 7-1). The geographic limits are part of the Patos-Mirim-Mangueira system, the largest costal lagoon system in the world (Santos et al. 2008), which was formed by successive sea level fluctuations during the Quaternary (Tomazelli et al. 2000). This hydrological system is composed of a series of interconnected lagoons and wetlands. The higher parts are characterized by pastures, remaining forests and dunes, while the lower portions are predominantly covered by natural and man-made wetlands (Schreiner et al. 2105).

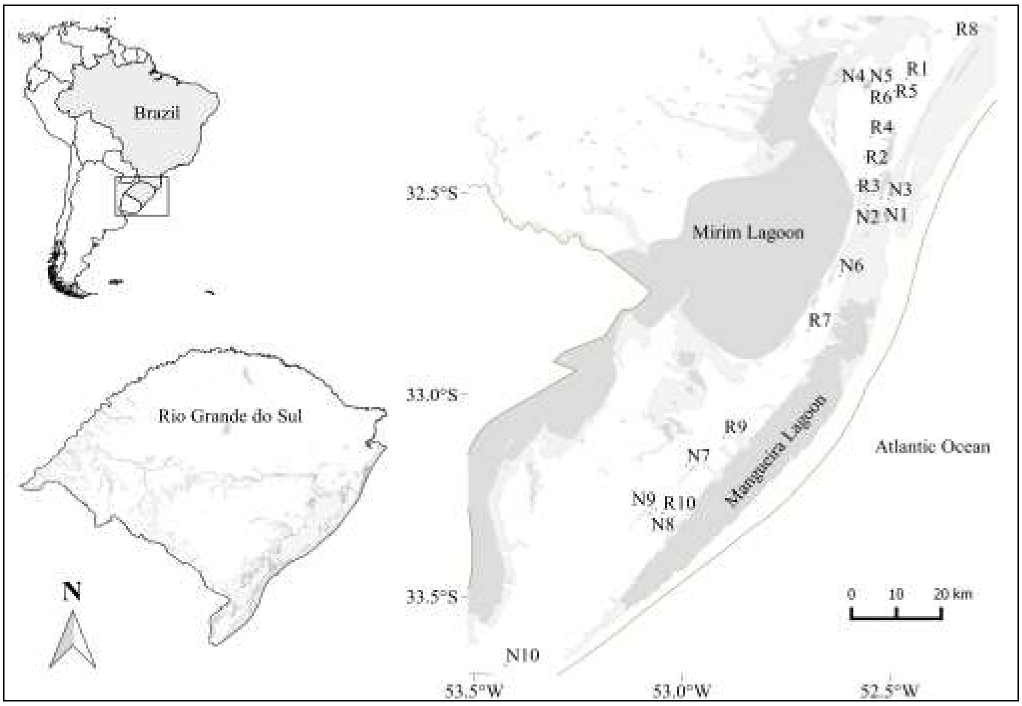

Fig. 7-1: Geographical limits of the studied area, and position of the 20 coastal wetlands. Abbreviations: N: natural wetlands; R: rice areas.

The natural wetlands are permanently flooded and covered by dense stands of aquatic macrophytes (Maltchik et al. 2004, Rolon et al. 2010). The rice fields are temporary in the landscape and are flooded by extensive irrigation for periods of approximately 90 days (Canterle et al. 2013). The sediment characteristics vary according to geology, morphology, and the surrounding areas of the aquatic ecosystems. In general, the sediment is composed of allochthonous sand depositions derived from the ocean or wind, associated with silt, clay and autochthonous deposits of organic matter (Schäfer 1992). The climate is humid subtropical according to the Köppen classification (Maluf 2000). Temperatures vary from 13.4ºC to 22.6ºC (minimum and maximum means, Reboita et al. 2006).

Field samples

Field samples of sediments were collected over three days, from 1 to 3 March 2016, from natural and rice crop wetlands before the end of the rice crop harvest in the last week of March (Canterle et al. 2013). The natural areas were chosen by the submerged condition and the presence of aquatic macrophyte stands, while rice areas were selected by the submerged condition and the presence of rice cultivation. In each wetland ecosystem (n = 20), four replicates (n = 4) of sediment samples were collected (Fig. 7-1), including natural (n = 10) and rice crops (n = 10). All sites were randomly selected in the landscape. Among the natural ecosystems, there were two areas (n4 and n5) situated inside a conventional rice cultivation (r6), and another two (n8 and n9) inside an organic rice cultivation (r10). These natural wetlands inside rice cultivations are characterized by the maintenance of aquatic macrophyte stands. In the field, we measured physicochemical characteristics of the water (pH and dissolved oxygen, DO) and water column depth with a calibrated probe (Horiba U-50®, Japan).

The sediment samples (top 5 cm of sediment) were randomly collected, using an acrylic sediment corer (50 cm long and Ø9 cm diameter). Samples were stored in plastic bags, refrigerated (4ºC) in dark containers and transported to the laboratory immediately after sampling. They were maintained in a refrigerator (5ºC) for a maximum period of seven days prior to the beginning of incubation. Water samples (500 ml) were collected in plastic bottles, refrigerated (4ºC) and maintained in a freezer until the beginning of incubation.

Experimental incubation

Sediment samples were transferred to borosilicate glass vials (30 ml) with a 10 ml plastic syringe, which had the tip cut off to increase width (Duc et al. 2010). The vials were hermetically closed and sealed with a thick (10 mm) large butyl rubber stopper, which was secured with an aluminum crimp seal. To avoid any oxygenation, the headspace was purged three times with N_2 gas creating an anoxic condition in the incubation vials (Duc et al. 2010, Marotta et al. 2014).

The experiment was conducted with four (n = 4) slurries for each wetland (n = 20), composed of sediment (5 g) and water (5 ml), which were incubated in vials in dark conditions under four controlled temperature levels (5, 15, 25 and 35ºC). Gas concentrations in the headspaces were monitored five times during the experiment (0, 7, 15, 30 and 90 days), amounting to 1360 vials. Before estimating the gas concentrations, the biological activity was stopped by acidification ($pH < 1.5$) by the addition of 2 ml of 10% sulfuric acid to each vial (Marotta et al. 2014). The CH_4 and CO_2 concentrations were measured within 24 hours after the end of each incubation using a gas chromatograph (Varian 450; GC, Netherlands) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The gas chromatograph was calibrated with certified standard gas (CH_4: 2 ppm, CO_2: 400 ppm).

Sediment characterization

Portions of the sediment samples were analyzed to characterize and compare the initial concentrations of CH_4 and CO_2. Interstitial water content (IW) was determined by the differences in weights of wet and dry samples using a precision balance. Sediment samples were dried and homogenized after the removal of any visible plant material to estimate the amount of organic matter (OM) and nutrients (TN and TOC). The total organic matter content

(OM) was estimated by ignition at 550ºC for 4 hours. Total organic carbon (TOC) was estimated by calculating the percentage of organic carbon (47%) in organic matter content (Westlake 1963). The elemental analyses of TN were determined by the Kjeldahl method according to Allen et al. (1974).

Statistical analyses

The carbon gas concentrations were considered dependent variables, while temperature and wetland type (natural and rice) were considered independent. Normality (Kolmogorov-Smirnov test), homogeneity of variance (Bartlett's test), and linearity were tested. The potential carbon gas production rates were transformed ($\log_{10}$) to minimize the variance, linearize the responses, and normalize the distribution.

The initial differences (time zero) among water column and sediment characteristics of natural and rice wetlands were tested with a Student's *t*-test. To summarize and facilitate visualization of the data patterns of the wetlands, we used principal component analysis (PCA) with a correlation matrix with means of all sediment and water column variables.

The CH_4 and CO_2 potential production rates were estimated by a linear regression of carbon gases concentration vs. incubations times (7, 15, 45 and 90 days). Time zero was not considered in the estimation due to the significantly higher concentration of CH_4 and CO_2 concentrations in relation to subsequent incubation times. The fourth time (90 days) was not considered when estimating the rates of CO_2 production, due to problems with the chromatograph TCD detector. The maximal slope of the linear regression was used to estimate the potential rates of gas production at each temperature. These rates minimize problems resulting from different time lags among different ecosystems and temperatures (Marotta et al. 2014).

To estimate and describe the relationship between CH_4 and CO_2 anaerobic production rates (mg $g^{-1}d^{-1}$) and temperatures (ºC) of the natural and rice wetlands, we used a simple linear regression. To test the differences between regression lines of natural and rice wetlands of CH_4 and CO_2 anaerobic production, we used the F-statistic. All statistical analyses were performed with R Software R-3.2.2 (R Core Team 2016).

Projections of GHG production

We estimated the percentage rise of gas production for a 30°C temperature range (5–35°C) and for 10°C intervals (5–15ºC, 15–25ºC, 25–35ºC). To estimate the change in potential production rates of carbon gases with increased temperature, we calculated the Q_{10} values (Duc et al. 2010). To estimate the effects of warming on the potential production rates of carbon gases in both types of wetlands, we used the linear regression equations of $\log_{10}$ CH_4 and CO_2 production rates vs. temperature: $\log_{10}(Y) = a+b*x$, where a is the Y intercept, b is the slope (potential rates of gas production,) x is the temperature (ºC) and Y is the rate of gas production in each wetland type (CH_4 production: $\log_{10}(\text{rice}) = 0.009 + 0.209 *$ Temperature; $\log_{10}(\text{natural}) = 0.0189 + 0.254 *$ Temperature; and CO_2 production: $\log_{10}(\text{rice}) = 0.572 + 5.358 *$ Temperature; $\log_{10}(\text{natural}) = 0.930 + 5.900 *$ Temperature). To estimate the effects of climate change, we used the IPCC conservative projections for 2100 (IPCC 2007), the scenarios B1 projects elevations between 1.1ºC and 2.9ºC. Thus, we added 1.1ºC and 2.9ºC to the maximal (22.6ºC) and minimal (13.4ºC) means of atmospheric regional temperatures (Reboita et al. 2006). As wetlands show low water column depth, we assumed maximal and minimal means of atmospheric temperatures.

Results

The water column and sediment characteristics of the natural and rice wetlands are shown in Table 7-1. Some important factors highlight differences among wetlands. First, dissolved oxygen concentrations in the water column were higher in rice wetlands ($p = 0.046$), as was water content in the interstitial sediment ($p < 0.001$). Second, natural wetlands showed higher means of organic matter ($p = 0.003$), nitrogen ($p = 0.043$) and carbon ($p = 0.002$) in the sediment. Third, in the headspace, carbon gas concentrations measured before the start of the experiment (time 0) did not show significant differences ($p > 0.05$) among rice and natural wetlands. However, mean CH_4 concentrations were relatively higher in rice wetland sediments (2.171 ± 1.126 mg L^{-1}), which showed lower means of CO_2 concentrations (31.729 ± 22.300 mg L^{-1}). In natural wetlands, the CH_4 and CO_2 concentrations were 1.560 ± 0.781 mg L^{-1} and 54.917 ± 48.175 mg L^{-1}, respectively.

When the carbon gas concentrations were related to environmental variables in the PCA, the first (40.56%) and second (18.02%) components explained 58.58% of the variation (Fig. 7-2). The first component corresponded to CH_4 concentration, interstitial water, dissolved oxygen concentrations, and separated natural and rice wetlands, according to their differences in these variables. The second component corresponded to CO_2, dissolved oxygen, nitrogen concentrations, and separated natural wetlands, which showed large dispersion in relation to rice wetlands. Wetland n9, which was inside the organic rice wetland (r10) contributed to this large distance among natural wetlands. On the other hand, the natural areas n4 and n5, located inside a conventional rice paddy (r6), were not so distant from the other natural areas (Fig. 7-2).

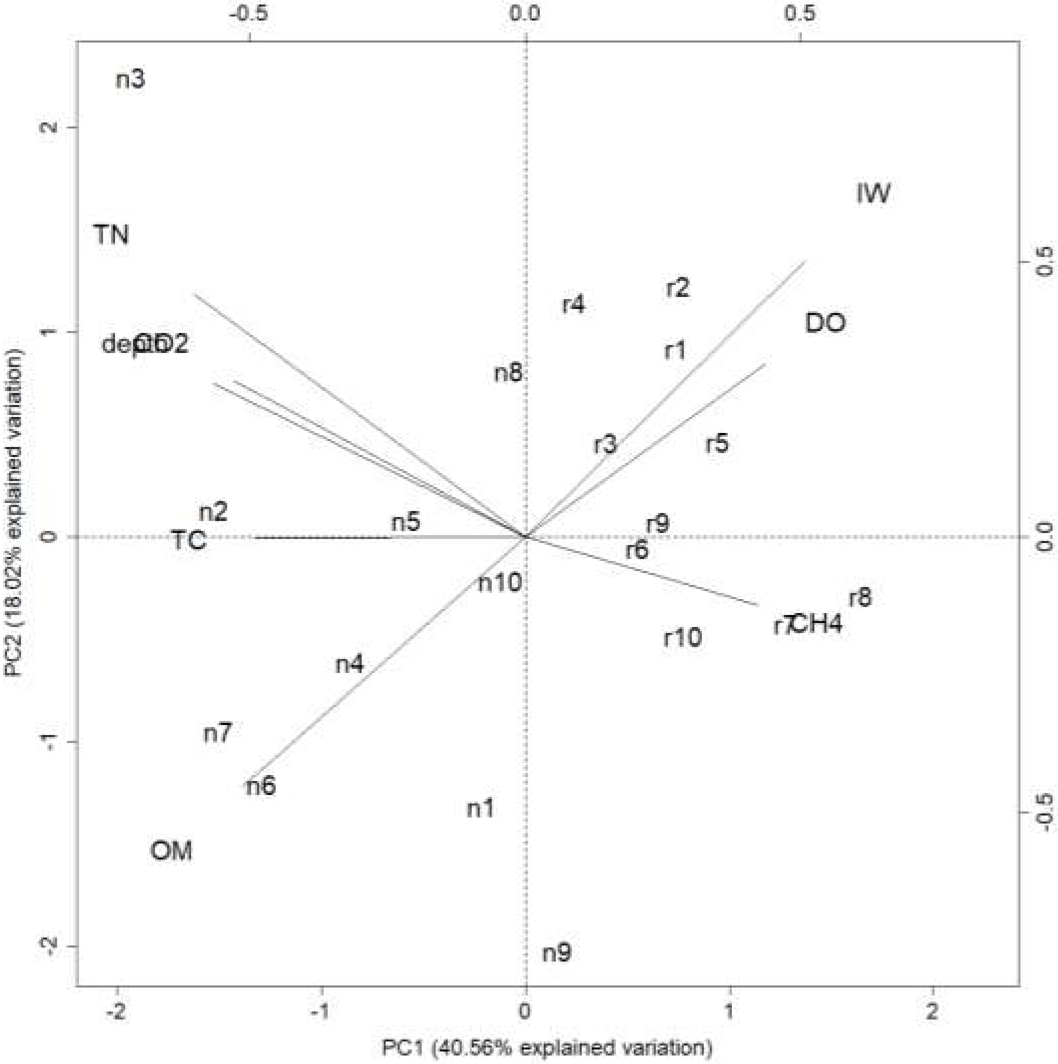

Fig. 7-2: Results of PCA of the CH_4 and CO_2 concentrations and environmental variables from the natural and rice wetlands. PC1 explains 40.56% of the variation and PC2 explains 18.02%. Abbreviations: OD: dissolved oxygen; TN: total nitrogen; TC: total carbon; MO: organic matter; IW: interstitial water; depth: water column depth; CO_2: carbon dioxide; CH_4: methane.

Table 7-1: Mean ± standard deviations (SD) of sediment variables: methane (CH_4), carbon dioxide (CO_2), organic matter (OM), interstitial water (IW), total nitrogen (TN), total carbon (TC) and water column variables measured in the field: depth, pH, dissolved oxygen (DO), and the p value of the Student's *t*-test of the differences among sediment and water column characteristics of natural and rice wetlands. Significant p values are in bold

	Sediment												**Water Column**				
	CH_4 ($mg.L^{-1}$)		**CO_2 ($mg.L^{-1}$)**		**OM (%)**		**IW (%)**		**TN (mmol/g)**		**TC (mmol/g)**		**Depth (m)**		**pH**		**D**
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Me**
r-1	1.366	1.118	15.405	11.311	14.524	2.852	69.689	2.125	0.254	0.017	5.689	1.117	0.130	0.027	5.736	0.212	8.6
r-2	1.014	0.640	22.364	15.403	12.467	1.418	69.069	2.265	0.389	0.216	4.883	0.555	0.120	0.027	6.254	0.153	8.5
r-3	1.622	0.442	31.383	15.753	11.435	1.314	61.770	6.586	0.301	0.108	4.479	0.515	0.200	0.035	6.510	0.132	6.0
r-4	2.677	0.759	78.670	56.901	15.886	5.429	74.888	1.638	0.298	0.072	6.222	2.126	0.220	0.057	6.268	0.276	6.9
r-5	2.635	1.198	43.131	32.381	15.146	2.274	67.761	1.771	0.221	0.099	5.932	0.891	0.120	0.027	6.154	0.108	8.2
r-6	1.117	1.410	44.289	15.745	13.464	4.504	74.293	6.479	0.118	0.051	5.274	1.764	0.120	0.027	6.982	0.129	5.4
r-7	2.998	1.693	26.965	25.294	16.627	2.424	70.516	3.258	0.050	0.029	6.512	0.949	0.100	0.000	7.220	0.195	7.3
r-8	3.306	1.694	10.571	8.873	13.803	3.530	76.189	3.726	0.070	0.050	6.391	2.220	0.100	0.000	7.462	0.300	7.8
r-9	2.095	0.356	31.576	35.094	18.447	11.371	63.640	11.315	0.265	0.059	7.225	4.454	0.100	0.000	7.698	0.339	8.1
r-10	2.883	1.948	12.933	6.249	20.538	4.484	62.587	3.715	0.217	0.037	8.044	1.756	0.110	0.022	7.818	0.090	7.9
Mean	2.171	1.126	31.729	22.300	15.802	3.966	69.040	4.288	0.218	0.074	6.065	1.635	0.142	0.022	6.810	0.193	7.5
n-1	0.674	0.368	17.779	7.112	24.518	8.433	42.370	9.295	0.494	0.084	9.603	3.303	0.140	0.065	5.930	0.126	6.6
n-2	0.531	0.287	82.258	45.817	26.232	3.914	44.507	16.322	0.653	0.123	10.274	1.533	0.180	0.115	5.786	0.137	6.9
n-3	0.863	0.630	81.721	97.285	23.904	9.013	64.200	13.279	0.236	0.039	9.362	3.530	0.490	0.022	6.170	0.181	7.7
n-4	1.912	1.321	47.983	56.281	19.954	5.925	39.909	8.972	0.279	0.080	7.815	2.320	0.330	0.057	6.656	0.121	6.0
n-5	3.015	0.787	101.312	48.365	16.557	1.720	52.338	2.515	0.360	0.077	6.485	0.674	0.230	0.104	6.190	0.108	5.1
n-6	1.749	1.189	42.201	30.435	31.064	5.844	41.887	9.931	0.378	0.043	12.167	2.289	0.330	0.115	6.110	0.222	5.0
n-7	1.524	0.922	65.404	76.741	28.013	10.792	52.373	15.768	0.355	0.285	10.972	4.227	0.164	0.035	7.458	0.238	4.0
n-8	1.450	0.764	40.815	62.885	16.858	9.014	69.406	2.575	0.099	0.079	6.603	3.531	0.150	0.000	7.774	0.148	7.5
n-9	1.910	0.766	14.777	8.651	30.298	6.267	41.669	3.865	0.350	0.084	11.867	2.454	0.130	0.057	7.684	0.162	7.7
n-10	1.974	1.095	21.272	12.562	14.825	7.598	49.379	8.054	0.223	0.025	5.806	2.975	0.110	0.022	6.824	0.342	6.9
Mean	1.514	0.781	54.917	48.175	23.222	6.852	49.804	9.058	0.343	0.092	9.095	2.684	0.225	0.059	6.658	0.178	6.3
p-value	p=0.102		p=0.103		**p=0.003**		**p< 0.0001**		**p=0.043**		**p=0.002**		p=0.069		p=0.065		

There were no significant differences in potential CH_4 (Fig. 7-3.a, CH_4: $p = 0.133$) and CO_2 (**Erro! Fonte de referência não encontrada.**.b, CO_2: $p = 0.232$) mean production rates among natural and rice wetlands, despite the relatively higher CO_2 and CH_4 formation rates in the headspace of natural wetlands sediments vials. However, potential CH_4 production rates in natural (CH_4: $F = 29.19$, $p < 0.0001$) and rice (CH_4: $F = 7.409$, $p = 0.0097$) wetlands, as well as potential CO_2 production rates in natural (CO_2: $F = 22.36$, $p < 0.0001$) and rice (CO_2: $F = 18.07$, $p < 0.0001$) wetlands, increased exponentially through the increased temperature gradient. The temperature sensitivity was predominantly higher at lower temperature intervals (5–15ºC; Table 7-2) with lower values at higher temperature intervals (25–35ºC; Table 7-2**Erro! Fonte de referência não encontrada.**). Considering the 10ºC intervals (Table 7-3), the lowest CH_4 (4.65%) and CO_2 (16.39%) potential production increases were observed in rice wetlands over 15–25ºC, while higher CH_4 (78.34%) and CO_2 (93.70%) increases were observed in rice (25–35ºC) and natural (15–25ºC) areas, respectively. Over the 30ºC temperature range (5–35ºC; Table 7-3), potential CH_4 production rates increased 155.29% in natural wetlands and 104.56% in rice wetlands, while potential CO_2 production rates increased 203.72% in natural wetlands and 229.01% in rice wetlands.

Table 7-2: The temperature sensitivity (Q_{10}) of carbon gas production rates, considering differences among 10°C temperature intervals (5–15ºC, 15–25ºC and 25–35ºC) in rice and natural wetlands.

	WETLAND	5-15º	15-25º	25-35º
CO_2	rice	0.060	0.109	0.000
	natural	0.405	0.003	0.005
CH_4	rice	0.672	0.515	0.000
	natural	0.198	0.005	0.006

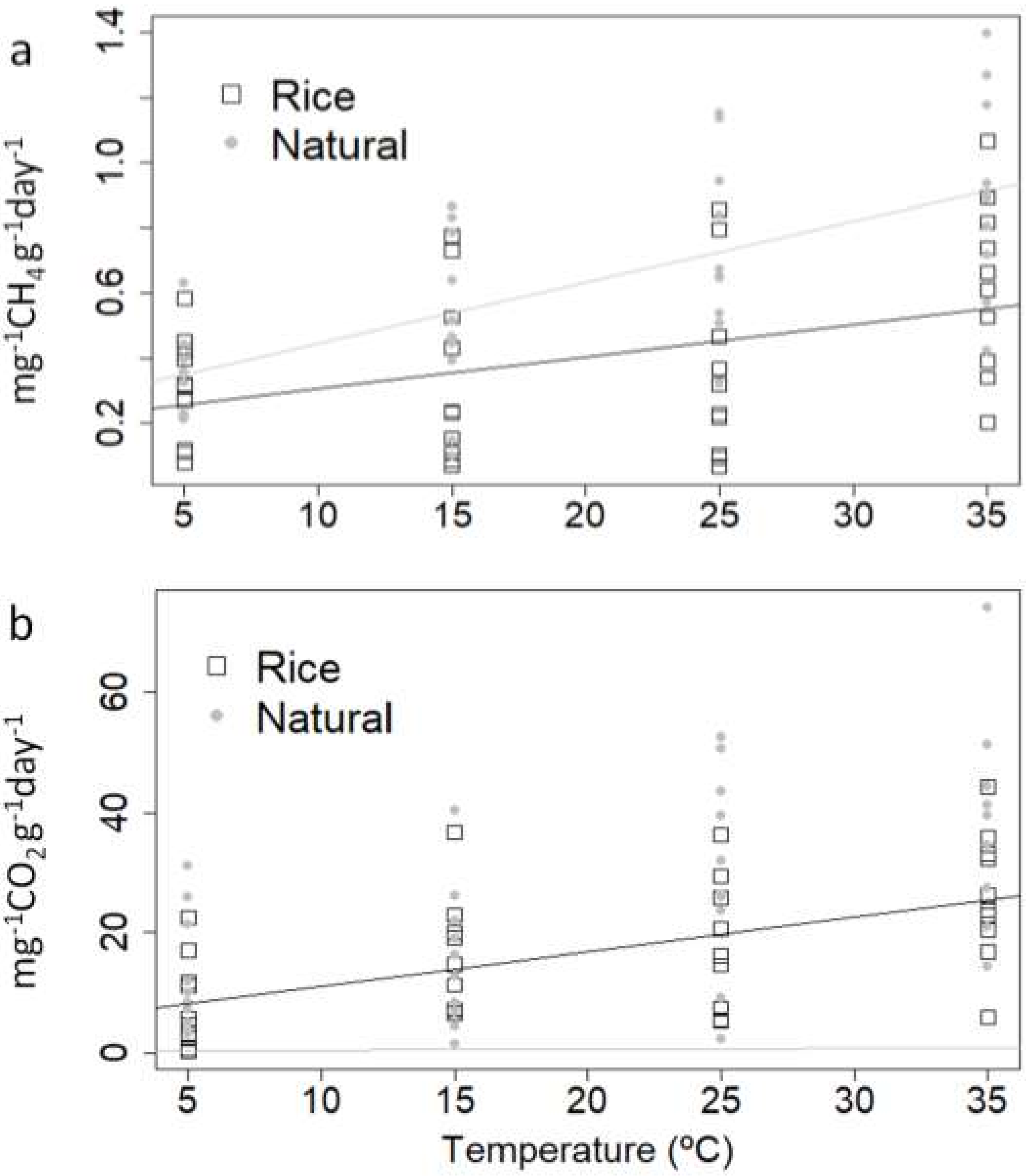

Fig. 7-3: Temperature variation of anaerobic CH_4 (a) and CO_2 (b) production rates in wetland sediments. Carbon gas production rates of natural (circles) and rice (squares) wetland sediments. Black (rice) and gray (natural) lines represent the fitted regressions ($p < 0.05$) for rice and natural sediments. Regression parameters of CH_4 production (A): $\log_{10}$(rice) = 0.009 + 0.209 * Temperature; $\log_{10}$(natural) = 0.0189 + 0.254 * Temperature. Regression parameters of CO_2 production (B): $\log_{10}$(rice) = 0.572 + 5.358 * Temperature; $\log_{10}$(natural) = 0.930 + 5.900 * Temperature.

Table 7-3: The percentage (%) of carbon gas production rates increases, considering differences 30ºC temperature range (5–35ºC), and the differences among 10°C temperature intervals (5–15ºC, 15–25ºC and 25–35ºC) in rice and natural wetlands.

	WETLAND	**5-35º**	**5-15º**	**15-25º**	**25-35º**
CO_2	rice	229.01	91.72	16.39	47.44
	natural	203.72	23.22	93.70	27.25
CH_4	rice	104.56	9.61	4.65	78.34
	natural	155.29	45.38	43.02	22.79

The percentage of CO_2 and CH_4 sediment potential production increased when associated with the temperature elevations of 1.1ºC and 2.9ºC, based on the scenario B1 of the IPCC projections (Table 7-4). Potential CO_2 production increased more in rice wetlands (4.54%) in lower temperature intervals. In addition, the percentage of CH_4 increase was greater than that for CO_2, with high values (18.91%) in rice wetlands, in periods of lower temperature means. The warming in periods of lower temperature means (13.4ºC) was greater in relation to the warming in periods of higher means of temperature (22.6ºC), mainly related to potential CH_4 production rates.

Table 7-4: The percentage (%) of carbon gas production rates according to IPCC projections associated with maximal (22.6ºC) and minimal (13.4ºC) means of regional atmosphere temperatures (Reboita et al. 2006).

		IPCC warming projections until 2100			
		+ 1.1ºC		**+ 2.9ºC**	
		23.7ºC	**13.4º**	**25.5º**	**16.4º**
CO_2	rice	0.99	1.83	2.50	4.54
	natural	0.96	1.78	2.45	4.42
CH_4	rice	3.05	7.61	7.75	18.91
	natural	2.71	6.38	6.87	15.84

Discussion

Initial concentrations of CH_4 and CO_2 were not significantly different in sediment samples from natural and rice wetlands, which contributes to the rejection of our first hypothesis. There could be some reasons for this: the organic matter content in wetlands sediments can be used in different ways by microorganisms, promoting variations in the CH_4 and CO_2 budgets (Sutton-Grier and Megonigal 2011, Canterle et al. 2013). In anoxic conditions, CH_4 is produced by methanogenic arechaea in the presence of labile organic material (Bastviken et al. 2004, Bodelier 2011). The microbial organic matter decomposition can result in CO_2, H_2, methanol, and acetate availability, which are important substrates for CH_4 production (Schulz and Conrad 1996, Bodelier 2011). The budget among CH_4 production in anaerobic conditions and the consumption at the anoxic–oxic boundary layer determines the CH_4 concentration in wetland sediments (Smith et al. 2003, Bodelier 2011, Marinho et al. 2015). Well-oxygenated conditions are favorable for methanogenesis inhibition (Kayranli et al. 2010, Petruzzellla et al. 2013), CH_4 consumption (Smith et al. 2003, Palma-Silva et al. 2013, Marinho et al. 2015) or CH_4 oxidation (Bastviken et al. 2004, Kayranli et al. 2010, Petruzzella et al. 2013) through the activity of methane oxidizing bacteria, which oxidize CH_4 through oxygen to produce CO_2. Moreover, oxygenated conditions can contribute to sink the CH_4 below the surface sediments (Kayranli et al. 2010).

The differences among aquatic macrophyte stands and detritus deposited above the sediment could be another important factor that contributes to the rejection of our first hypothesis. The presence of aquatic macrophytes can be the main autochthonous source of organic detritus accumulation (Furlanetto et al. 2012, Marinho et al. 2015). The roots of wetland plants may exude carbon that can be mineralized to CO_2 or other substrates to methanogenesis (Bodelier 2011), resulting in high CH_4 concentrations (Inglett et al. 2012, Cunha-Santino and Bianchini 2013, Petruzzella et al. 2013). Moreover, transport of oxygen in the roots and tissues may change the availability of oxygen in the sediment, resulting in methanogenesis suppression (Bastviken et al. 2004, Sutton-Grier and Megonigal 2011) or CH_4 oxidation (Bodelier 2011). Even with the reduction in abundance and biomass of aquatic macrophytes typical of rice cultivation practices (Rolon et al. 2010), the difference among detritus accumulation was not significantly different between initial CH_4 and CO_2 concentrations among wetlands. This has been demonstrated in previous experiments with anoxic sediment compared at different sites (Canterle et al. 2013).

Nutrient availability is an important factor in carbon degradation because it affects CH_4 cycling in wetland sediments (Kim et al. 2015). The addition of nitrogenous fertilizers (i.e., nitrate) can promote direct competition for electron acceptors leading to lower availability of substrates for methanogenic bacteria, resulting in lower CH_4 concentrations below the surface sediments (Bodelier 2011). On the other hand, application of inorganic fertilizer can promote favorable conditions for methanogenesis in rice wetland sediments (Canterle et al. 2013). Thus, higher nitrogen concentrations can result in competition for electron acceptors, resulting in lower CH_4 concentrations in natural wetlands. In rice fields, the fertilizer addition may enable methanogenesis, promoting higher initial CH_4 concentrations in these wetland sediments.

Temperature was the main factor influencing anaerobic organic carbon mineralization in both wetlands, corroborating our second hypothesis. At low temperatures, the establishment of anoxic conditions may stimulate the consumption of alternative electron acceptors that could promote low mineralization rates (Segers 1998, Duc et al. 2010).

Temperature elevation (≥30ºC) intensifies microbial activity, enhancing the supply of organic substrates and rapid depletion of lower electron acceptor concentrations favorable for substantial increases in the rates of carbon gas production (Segers 1998, Liikanen et al. 2002, Duc et al. 2010). Higher temperatures can promote an increase in CH_4 production from CO_2 and H_2, alternatively from acetate, which can result in CO_2 consumption by methanogenic bacteria, resulting in lower rates of CO_2 in relation to CH_4 (Schulz and Conrad 1996). Therefore, warmer temperatures are positively related to increases in the rates of electron acceptor reduction, which may result in lower electron acceptor concentrations, a favorable condition for CH_4 production (Segers 1998).

The temperature sensitivity for potential carbon gases production was higher in lower temperature intervals (Table 7-2). When we estimated the sediment potential gas production rates in intervals of 10ºC (Table 7-3), CH_4 increased more in natural wetlands at 25–35ºC, while CO_2 was higher in rice wetlands at 15–25ºC. Only natural wetlands showed higher CO_2 increases in the interval corresponding to the regional mean temperature (15–25ºC). In lake sediments from the littoral zone in Sweden, Duc et al. (2010) showed a more drastic increase in CH_4 formation between 20 and 30ºC, which would result in large emission of CH_4 production in the sediment (Duc et al. 2010). In the southern Brazil coastal plain, a variation of almost 10ºC is sufficient to significantly alter CH_4 concentrations in shallow lakes (Marinho et al. 2009), which, due to its association with shallow water column depth, could play an important role in CH_4 emission (Palma-Silva el al. 2013, Marinho et al. 2015). Not all gases produced in the sediment can reach the atmosphere, but sediment production rates determine the potential for subsequent atmospheric emissions and climate feedback (Marotta et al. 2014).

Our estimates of atmospheric warming by 2100, according to the IPCC B1 scenario (Table 7-4), indicated three important factors. First, elevation in the means of atmospheric temperature may promote higher rates of CH_4 than CO_2 production rates. Second, lower temperature means showed higher percentages of potential carbon gas production than higher temperature means. Third, the rates of potential carbon gas production may increase more in rice wetlands than natural wetlands. Not all the produced gas will reach the atmosphere, but higher potential CH_4 production rates relative to CO_2 suggest a powerful positive feedback on global warming, when the produced gas is emitted (Marotta et al. 2014), once the CH_4 radiative forcing is greater than CO_2 (IPCC 2007). Moreover, temperature and system characteristics (depth, productivity, and macrophyte abundance) are important for CH_4 fluxes, which affect emissions under experimental and field conditions (Natchimuthu et al. 2014). Thus, a higher temperature response of CH_4 relative to CO_2 in rice wetlands suggests that changes in the landscape may promote a more powerful positive climatic feedback.

Land use and climate change are likely to directly impact ecosystem processes through their influence on plant community composition (Sutton-Grier and Megonigal 2011), organic carbon loading and cycling in wetlands (Stern et al. 2007, Mitsch et al 2013), and nutrient availability in wetlands (Kim et al. 2015). In North American wetlands, Bridgham et al. (2006) reported that land-use changes have had the largest effects on carbon fluxes and consequent warming potential. Moreover, agricultural expansion may promote changes in wetland systems (Rolon et al. 2010), which represents an important anthropogenic source of CO_2 and CH_4 emissions (Canterle et al. 2013) and climate change (Mitsch et al 2015). However, some strategies in rice crops can reduce gas fluxes. For example, the management of water table levels may reduce CH_4 fluxes and decrease global warming potential of rice paddy fields (Meijide et al. 2017). Thus, the suppression of natural wetlands would change the vegetal composition, contributing to elevating carbon gas production and possible emission of these gases to the atmosphere, but effective strategies can mitigate this threat.

Despite the absence of differences among initial concentrations and production rates of carbon gases, warming promoted elevation in potential production rates of CH_4 and CO_2 in both natural and rice wetland ecosystems, mainly in periods of lower temperatures means. Thus, the maintenance of natural wetlands can contribute to being a sink for gases within the sediment, mainly CH_4.

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8 CONSIDERAÇÕES FINAIS E PERSPECTIVAS

O estudo demonstrou que conhecer as diferentes etapas do balanço do carbono é fundamental para avaliar os processos e projetar potenciais mudanças nos processos ecossistêmicos. A matéria orgânica e a produção autóctone representaram fatores inerentemente relacionados com as concentrações de metano na coluna da água, dos sistemas lóticos e lênticos. Outros aspectos relacionados com as maiores taxas de mineralização da matéria orgânica no sedimento das áreas alagadas, e com o tamanho dos corpos hídricos, também, apresentam relação positiva com as concentrações de CH_4. Os grandes corpos hídricos, principalmente os distribuídos nas áreas não urbanas, apresentaram concentrações de CH_4 relativamente menores, em relação aos pequenos lagos, encontrados principalmente nas áreas urbanizadas, que apresentaram predomínio de condição mais eutrófica.

As áreas alagadas não apresentaram diferenças significativas entre as taxas de produção, de CO_2 e de CH_4, apesar do maior acúmulo de matéria orgânica no sedimento das áreas naturais. A elevação da temperatura promoveu aumento significativo das taxas mineralização da matéria orgânica, principalmente de CH_4 nos sedimentos de rizicultura. As taxas de mineralização não diferiram significativamente entre os sistemas naturais e de rizicultura, no entanto, o aquecimento atmosférico projetado para os próximos 100 anos, está associado, a um aumento potencial da produção de CH_4 nas áreas de rizicultura.

As maiores taxas de mineralização associadas ao aquecimento atmosférico e as concentrações de CH_4 mais elevadas nos corpos hídricos urbanos, corroboram a influência do fator antrópico sobre o balanço dos gases de carbono. A alteração das características do entorno ou ocupação do solo, podem indicar maiores taxas de produção, e consequente aumento nas concentrações no sedimento e na coluna da água, principalmente com elevação da temperatura. O arroio urbano estudado nasce em uma área de banhados, passa por uma densa vegetação ripária e por áreas urbanizadas, aparentemente estas características estão relacionadas as altas concentrações do gás CH_4 encontradas.

Estudos recentes têm demonstrado a efetiva participação dos sistemas lóticos no balanço do carbono, que vai além do transporte dos sistemas terrestres para os sistemas costeiros. Ao longo do contínuo de ecossistemas aquáticos, o carbono sofre importantes transformações e volumes significativos tanto de CO_2 como de CH_4 podem ser retidos e ou emitidos para a atmosfera.

A partir dos resultados encontrados abre-se a perspectiva de novos estudos para avaliar a participação dos sistemas lóticos no balanço do carbono. Explorar, a capacidade de transformação do carbono orgânico, desde as áreas alagadas (nascentes), avaliando a contribuição da vegetação ripária e as taxas de emissão ao longo do contínuo até as áreas costeiras estuarinas.

A participação dos ecossistemas aquáticos do extremo sul brasileiro ainda é subestimada em nível global. Estudos futuros devem melhorar a compreensão sobre os processos que controlam as transformações do carbono nos ambientes aquáticos da região. As taxas de produção dos gases estufa nos diferentes ecossistemas devem ser estimadas de forma precisa, assim como os inputs de matéria orgânica, e as taxas de transformação e emissão de carbono para a atmosfera. O avanço no conhecimento e a compreensão do funcionamento dos sistemas aquáticos são importantes ferramentas para subsidiar estratégias de conservação dos ecossistemas aquáticos e mitigação fatores associados as mudanças climáticas.

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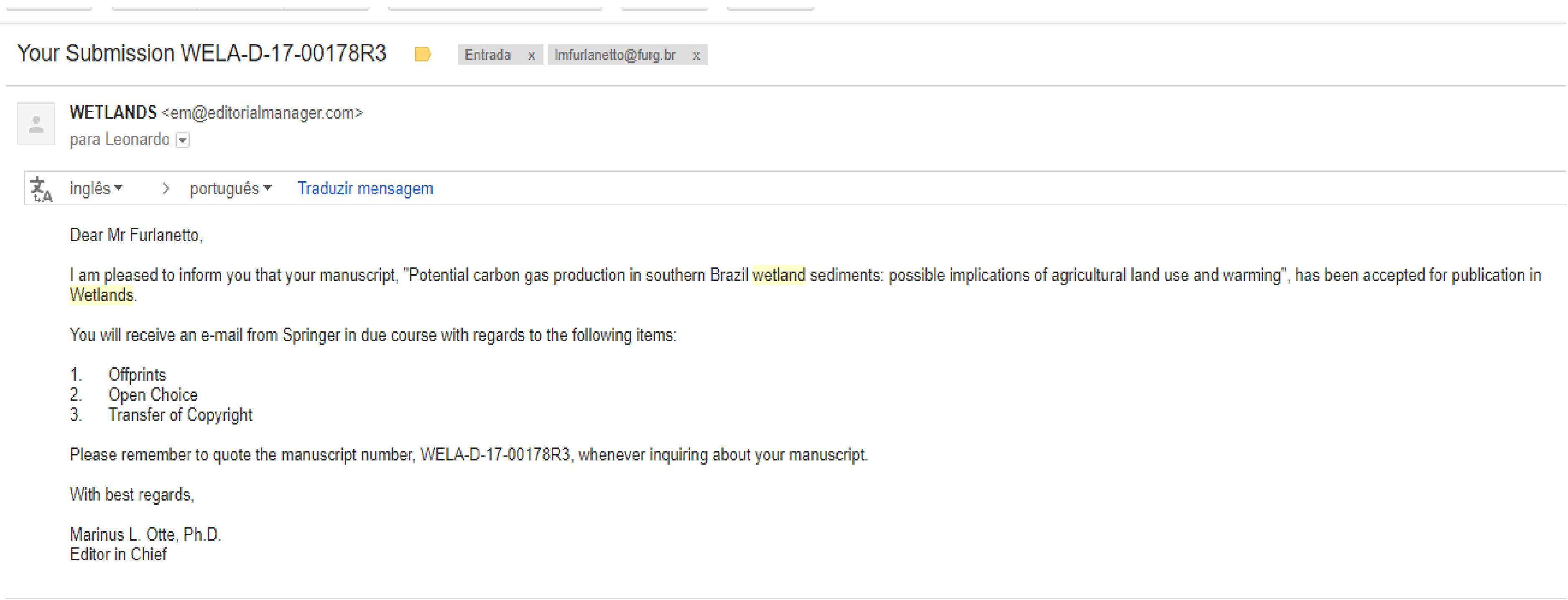
10 ANEXOS



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