UNIVERSIDADE FEDERAL DO PARANÁ

VIVIANE KORRES BISCH

COMPOSIÇÃO ELEMENTAR E ISOTÓPICA DA MATÉRIA ORGÂNICA DA BAÍA DO ALMIRANTADO (ANTÁRTICA) E A COMPREENSÃO DO CICLO DO CARBONO SEDIMENTAR LOCAL

PONTAL DO PARANÁ
2024

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Dissertação apresentada como requisito parcial à obtenção do grau de Mestre em Sistemas Costeiros e Oceânicos, no Curso de Pós-graduação em Sistemas Costeiros e Oceânicos.
Setor: Campus Pontal do Paraná, Centro de Estudos do Mar, Universidade Federal do Paraná.

Orientador: Prof. Dr. César de Castro Martins

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No dia dezoito de janeiro de dois mil e vinte e quatro às 09:00 horas, na sala Remoto - https://meet.google.com/veb-zcfp-ocp, CEM - UFPR, foram instaladas as atividades pertinentes ao rito de defesa de dissertação da mestranda **VIVIANE KORRES BISCH**, intitulada**: COMPOSIÇÃO ELEMENTAR E ISOTOPICA DA MATÉRIA ORGÂNICA DA BAIA DO ALMIRANTADO (ANTÁRTICA) E A COMPREENSÃO DO CICLO DO CARBONO SEDIMENTAR LOCAL.**, sob orientação do Prof. Dr. CÉSAR DE CASTRO MARTINS. A Banca Examinadora, designada pelo Colegiado do Programa de Pós-Graduação SISTEMAS COSTEIROS E OCEÂNICOS da Universidade Federal do Paraná, foi constituída pelos seguintes Membros: CÉSAR DE CASTRO MARTINS (UNIVERSIDADE FEDERAL DO PARANÁ), TAILISI HOPPE TREVIZANI (UNIVERSIDADE DE SÃO PAULO), MICHEL MICHAELOVITCH DE MAHIQUES (UNIVERSIDADE DE SÃO PAULO). A presidência iniciou os ritos definidos pelo Colegiado do Programa e, após exarados os pareceres dos membros do comitê examinador e da respectiva contra argumentação, ocorreu a leitura do parecer final da banca examinadora, que decidiu pela APROVAÇÃO. Este resultado deverá ser homologado pelo Colegiado do programa, mediante o atendimento de todas as indicações e correções solicitadas pela banca dentro dos prazos regimentais definidos pelo programa. A outorga de título de mestra está condicionada ao atendimento de todos os requisitos e prazos determinados no regimento do Programa de Pós-Graduação. Nada mais havendo a tratar a presidência deu por encerrada a sessão, da qual eu, CÉSAR DE CASTRO MARTINS, lavrei a presente ata, que vai assinada por mim e pelos demais membros da Comissão Examinadora.

Pontal do Paraná, 18 de Janeiro de 2024.

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TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação SISTEMAS COSTEIROS E OCEÂNICOS da Universidade Federal do Paraná foram convocados para realizar a arguição da dissertação de Mestrado de **VIVIANE KORRES BISCH** intitulada: **COMPOSIÇÃO ELEMENTAR E ISOTOPICA DA MATÉRIA ORGÂNICA DA BAIA DO ALMIRANTADO (ANTÁRTICA) E A COMPREENSÃO DO CICLO DO CARBONO SEDIMENTAR LOCAL.**, sob orientação do Prof. Dr. CÉSAR DE CASTRO MARTINS, que após terem inquirido a aluna e realizada a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa.
A outorga do título de mestra está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

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Obrigada!

I am not an island.
I am not alone.
I am my intentions
Trapped here in this flesh and bone

– Melissa Etheridge

RESUMO

A composição elementar e os isótopos estáveis na matéria orgânica (MO) sedimentar são importantes ferramentas geoquímicas de informação sobre os ambientes, os processos físicos e biogeoquímicos e até das condições paleoclimáticas da Terra. Sendo a região da Península Antártica uma das poucas áreas relativamente preservadas do planeta, sensível às mudanças climáticas e, ainda assim, o continente mais inexplorado da Terra, o presente trabalho trouxe como objetivo realizar a caracterização elementar e isotópica de sedimentos de diferentes regiões da Baía do Almirantado, Ilha Rei George, Antártica, a fim de avaliar as possíveis fontes de MO para a região. A malha amostral foi dividida em três partes: (i) 17 amostras de sedimento surficial espalhadas ao longo da Baía, coletadas em janeiro de 2020; (ii) Amostras superficiais coletadas ao longo da década de 2009–2019 em três pontos específicos (um na enseada Ezcurra, um na Mackelar e um na Martel), e; (iii) três testemunhos sedimentares curtos, coletados um em cada enseada entre 2007–2008. Um analisador elementar Thermo-Finnigan IRMS Delta V Plus foi empregado para a determinação dos isótopos estáveis de carbono ($\delta^{13}C$) e de nitrogênio ($\delta^{15}N$), conteúdo de carbono orgânico total (COT) e nitrogênio total (NT). As análises granulométricas foram realizadas utilizando um aparelho laser Malvern Hydro 2000, após a descarbonatação e remoção de MO. Os resultados indicam que a matéria orgânica nos sedimentos da enseada Ezcurra tem origem principalmente em plantas terrestres prevalentes na Antártica, como musgos e líquens, e aquáticas. Da mesma forma, a enseada Mackelar destacou-se com significativas contribuições das fontes mencionadas anteriormente, além de algas. Em contraste, a enseada Martel exibiu amplo e diversificado tipos de fontes, predominantemente influenciadas por contribuições de musgos, líquens e por excrementos de animais, como diversos mamíferos e aves marinhas. Sedimentos mais recentes, coletados após 2008, indicaram menor contribuição de fontes animais na enseada Martel e musgos e líquens emergem como as fontes predominantes, espelhando os padrões observados nas outras enseadas. As conclusões deste estudo fornecem informações inéditas sobre o aporte de matéria orgânica aos sedimentos na Baía do Almirantado, indicando mudanças ao longo da escala de tempo estudada.

Palavras-chave: Testemunhos sedimentares. Sedimentos superficiais. Isótopos estáveis de carbono. Isótopos estáveis de nitrogênio. Baía do Almirantado.

ABSTRACT

The elemental composition and stable isotopes in the sedimentary organic matter (OM) are important geochemical tools for understanding environments, physical and biogeochemical processes, and even paleoclimatic conditions on Earth. Once the Antarctic Peninsula region is one of the few relatively preserved areas on the planet, sensitive to climate change, and yet remains the most unexplored continent, this study aimed to characterize the elemental and isotopic composition of marine sediments from different regions of Admiralty Bay, King George Island, Antarctica, to assess potential sources of OM. The sampling included: (i) 17 surficial sediment samples collected across the bay in January 2020; (ii) Surficial samples sampled during the 2009–2019 period at three specific sites (one in Ezcurra inlet, another in Mackelar inlet, and the last one in Martel inlet), and; (iii) three sediment cores collected from each inlet of the bay in 2007-2008. A Thermo-Finnigan IRMS Delta V Plus elemental analyzer was applied to determine stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopes, total organic carbon (TOC), and total nitrogen (TN). Grain size analyses used a Malvern Hydro 2000 laser, after carbonates and OM removal. OM in sediments from Ezcurra inlet, primarily originates from terrestrial plants prevalent in Antarctica, such as mosses and lichens, and aquatic ones. Similarly, Mackelar inlet is highlighted by significant contributions from these two above mentioned sources, as well as algae. In contrast, Martel inlet exhibits a diverse range of sources, predominantly influenced by various marine mammals and seabirds and their excrements, incorporating signals from mosses and lichens. However, recent sediments sampled post-2008 in Martel inlet, show a decreased contribution of animal sources, and mosses and lichens emerging as the predominant sources, corroborate patterns observed in the other inlets. The findings of this study provide unprecedented information about the input of OM to sediments in Admiralty Bay, indicating changes over the time scale studied.

Key-words: Sediment core. Surficial sediments. Stable carbon isotope. Stable nitrogen isotope. Admiralty Bay.

SUMÁRIO

1. Contextualização geral

A composição elementar e os isótopos estáveis da matéria orgânica (MO) sedimentar são importantes ferramentas geoquímicas de informação sobre os ambientes, os processos físicos e biogeoquímicos e até das condições paleoclimáticas da Terra (Corbett et al., 2015). São utilizadas para a investigação do ciclo de elementos químicos e da MO presente nos diferentes compartimentos do planeta, fluxos energéticos de cadeias alimentares, vias de ciclagem de nutrientes e o predomínio das diversas fontes de MO em diferentes escalas de tempo (Schulz e Zabel, 2006).

A forma elementar do carbono e do nitrogênio, bem como as razões entre seus respectivos isótopos estáveis, são indicadores (*proxies*) geoquímicos estudados no ambiente marinho, pois estão diretamente associados ao ciclo da MO marinha e terrígena (Carrizo et al., 2019). Esses elementos estão distribuídos em diferentes compartimentos através da formação, aporte e degradação da MO que irá, eventualmente, compor o sedimento. Por isso, a determinação da composição elementar e isotópica no pacote sedimentar de uma região fornece informações relevantes quanto ao ciclo desses elementos, sua fonte e a variabilidade espaço-temporal.

Quando há a transferência destes elementos entre esses compartimentos através de processo físicos, químicos e biológicos, há um fracionamento isotópico, resultando em uma assinatura específica quanto a distribuição de isótopos estáveis na MO dos diferentes compartimentos do ecossistema. A partir dessa assinatura, representada pela razão isotópica (δ), é possível obter informações sobre a fonte de carbono ou de nitrogênio que compõe a MO (Schulz e Zabel, 2006).

A abundância isotópica referente a quantidade de carbono existente na Terra, é cerca de 1,1% de ^{13}C e de 98,9% ^{12}C. O valor da razão $\delta^{13}C$ da MO é medido em relação ao padrão *Pee Dee Belemnite* (PDB) (0,0 ‰) e por isso os valores apresentados são negativos, sendo utilizadas as denominações ‘enriquecido’ ou ‘empobrecido’ em ^{13}C (O'Leary, 1981; Peters et al., 2005; Freeman e Pancost, 2014).

A identificação da MO pela a razão entre os isótopos ^{13}C e ^{12}C ($\delta^{13}C$) é, tradicionalmente, feita em relação a discriminação do $^{13}CO_2$, por parte do metabolismo dos tipos de vegetação que realizam a fotossíntese (O'Leary, 1981; Muccio e Jackson, 2009; Freeman e Pancost, 2014).

As plantas C3 utilizam 3 carbonos através do Ciclo de Calvin-Benson (pela enzima rubisco), as plantas C4 utilizam 4 carbonos através do Ciclo de Hatch-Slack (ácido málico) e as plantas CAM (como as plantas suculentas) tem o Metabolismo Ácido de Crassulácea, que utiliza os dois mecanismos anteriores, sendo o primeiro na presença de luz e o segundo no escuro, estabelecendo uma maior ou menor discriminação do $^{13}CO_2$, resultando em MO com uma maior faixa de variação ($\delta^{13}C$, -13 a -25‰) em comparação com as plantas C3 (-28,0 ± 2,5‰) e C4 (-13,0 ± 1,5‰) (Chikaraishi, 2014).

O ciclo do nitrogênio marinho é inerentemente mais complexo do que o ciclo do carbono; os múltiplos estados de oxidação do nitrogênio inorgânico e a multiplicidade de vias biológicas que interconectam diferentes reservatórios de nitrogênio muitas vezes tornam difícil identificar os processos-chave que controlam o movimento do nitrogênio através dos ecossistemas (Schulz e Zabel, 2006). Os autores ainda trazem que as principais transformações biológicas do nitrogênio em sistemas marinhos incluem a utilização das formas dissolvidas de nitrogênio inorgânico (NO_2^-, NO_3^- e NH_4^+) pelo fitoplâncton, o consumo de fitoplâncton pelos consumidores primários e a remineralização do nitrogênio orgânico por animais e bactérias.

Ainda segundo os mesmos autores, as entradas do nitrogênio para os oceanos são, principalmente, precipitação, descarga continental e fixação do N_2 atmosférico, esta última realizada por bactérias e algas marinhas responsáveis por fixar esse nitrogênio atmosférico e transformá-lo em orgânico. Existe, então, a eventual decomposição dessa matéria orgânica, onde é produzida amônia (NH_4^+) e a nitrificação, realizada por organismos chamados organismos nitrificantes. Essa remoção biológica de nitrogênio ocorre em duas etapas, sendo a primeira a oxidação de NH_4^+ a NO_2^- e a segunda a oxidação do NO_2^- a NO_3^- (Schulz e Zabel, 2006). O nitrogênio é removido dos oceanos pelo soterramento nos sedimentos e através da denitrificação, que ocorre principalmente no fundo marinho, onde há menor disponibilidade de oxigênio. Esta remoção da coluna d'água é o balanço da fixação de nitrogênio, uma vez que converte o NO_3^- em nitrogênio gasoso.

O $\delta^{15}N$ é uma importante ferramenta que permite estimar mudanças na dinâmica dos nutrientes na coluna d'água, uma vez que a transferência do nitrogênio pela teia trófica conta com uma particularidade que é um enriquecimento de 3.5‰ de 15N a cada nível trófico (Chikaraishi, 2014).

Trabalhos pioneiros na utilização de isótopos então utilizam a razão do nitrogênio como proxy complementar da $\delta^{13}C$, e também fizeram uso da razão entre os teores de carbono orgânico total (COT) e nitrogênio total (NT), chamada de razão COT/NT (ou simplesmente C_{org}/N), para auxiliar na identificação da origem da fonte da MO, onde valores específicos desta razão podem indicar fontes distintas ($C_{org}/N < 6$: autóctone: fito- e zooplâncton; $C_{org.}/N \sim 10{,}0$: autóctone de deposição recente, e; $C_{org}/N > 15{,}0$: alóctone) (Meyers, 1994).

Contudo, as faixas de variação da razão isotópica da MO na Antártica são significativamente diferentes daqueles encontrados em outras partes do mundo. Galimov (2000) analisou amostras de plantas coletadas em diversos lugares, inclusive nas Ilhas Shetlands do Sul, e encontrou valores diferentes de $\delta^{13}C$ de líquens e musgos antárticos daqueles descritos para regiões tropicais e temperadas. Da mesma maneira, os valores para o fitoplâncton antártico são diferentes, uma vez que existem particularidades controles da composição isotópica de carbono do fitoplâncton do Oceano Antártico e faz referência à variabilidade isotópica ao longo das diferentes latitudes (Popp et al., 1999).

A região da Península Antártica é considerada uma das poucas áreas relativamente preservadas do planeta, uma das áreas mais sensíveis às mudanças climáticas e, ainda assim, o continente mais inexplorado da Terra (Carrizo et al., 2019). A descrição e o entendimento da composição elementar e isotópica em sedimentos da região da Antártica marítima (segundo classificação climática de Schwerdtfeger, 1970) é limitada a poucos estudos.

A Antártica é um laboratório natural único para a pesquisa da poluição global e é ideal para a realização de estudos sobre a contaminação ambiental. Além disso, o impacto humano no ambiente antártico intensifica os processos relacionados à mudanças climática, e mesmo levando em consideração todas as obrigações das atividades humanas e as diretrizes rigorosas do Protocolo de Proteção Ambiental do Tratado da Antártica (Bargagli, 2008, Szopinska et al., 2019), os ecossistemas antárticos têm enfrentado uma crescente pressão humana por pelo menos seis décadas (Bargagli, 2008).

Este fato reforça a relevância de se realizar estudos exploratórios focados na determinação elementar e isotópica de carbono e nitrogênio, que, indiretamente, fornecerão informações para a compreensão dos ciclos biogeoquímicos locais e para o entendimento da dinâmica de substâncias antropogênicas na área. Tal caracterização também é importante para o entendimento das mudanças ambientais no presente (Bae et al., 2021).

A Baía do Almirantado, na Ilha Rei George, é a maior baía do arquipélago das Ilhas Shetlands do Sul, localizado na Península Antártica (Combi et al., 2017). Na região, isótopos estáveis ainda são muito pouco estudados, principalmente na matéria orgânica sedimentar. Ela é um dos ecossistemas marinhos mais pesquisados da Antártica, devido aos Programas Antárticos Polonês e Brasileiro, que conduzem estudos científicos na área há cerca de 40 anos. No entanto, ainda há um vasto campo para aprendizado (Gheller e Corbisier, 2022).

Em uma revisão da literatura regional, nota-se que pesquisas envolvendo isótopos estáveis na Antártica aborda desde conteúdo de carbono e nitrogênio em solo, musgo e tapete microbial aquático (Galimov, 2000, Wang et al., 2000, Liu et al., 2006), até razões isotópicas em bentos para investigação de teias alimentares (Corbisier et al., 2004) em diatomáceas (Bae et al., 2021) ou em ambientes adjacentes, como lagos na Península Antártica (Carrizo et al., 2019). Contudo, até onde se pesquisou, informações dos sedimentos marinho são escassos.

Alguns estudos descreveram as fontes de MO na Baía do Almirantado através de outros indicadores geoquímicos, como o ferro (Sierpinski et al., 2023), marcadores orgânicos como os isoGDGTs (Dauner et al., 2021) e hidrocarbonetos alifáticos (Martins et al., 2021). Os trabalhos sobre a composição molecular de sedimentos ao longo das últimas cinco décadas sugerem uma miscelânia de fontes aquáticas e terrestres de carbono orgânico em sedimentos superficiais, com influência de macrófitas aquáticas, musgos, líquens, e variação da predominância terrígena ou marinha dependendo da enseada e do período avaliado.

Esse histórico de conhecimento construído sobre a dinâmica da MO na região da Península Antártica permite aperfeiçoar a compreensão do clima, flora e fauna local. Durante o inverno austral, a Baía do Almirantado permanece coberta por gelo, e a troca de CO_2 entre água e atmosfera pode ser restrita. Nessa condição, a dissolução do carbonato nos sedimentos de fundo é mínima; então observa-se maiores valores de carbonato no sedimento (Yoon et al., 2000). Ao mesmo tempo, as baixas temperaturas ampliam a cobertura da superfície do mar, limitando a produtividade primária e restringindo o aporte continental, o que reduz o conteúdo de COT que chega aos sedimentos de fundo.

No verão austral, a Baía do Almirantado passa por um aumento da temperatura do ar que, gerando derretimento do gelo e maior precipitação, aumentando o aporte terrígeno para o mar (Yoon et al., 2000). Esse aporte, junto com maior estratificação da coluna d'água gerada pela água doce, tanto de geleira quanto da chuva, permite maior produtividade primária marinha. Com isso, há uma menor razão C_{org}/N, associada à produção de MO autóctone e menor carbonato, por conta do afundamento da profundidade de dissolução de carbonato.

Na parte terrestre, o aumento da temperatura no verão austral pode deixar o solo exposto pelo derretimento do gelo e, com isso, favorecer o crescimento de plantas terrestres como musgos e líquens (Martins et al., 2021). Além disso, existem colônias de pinguins que vivem nas regiões costeiras sem gelo, e que fazem a transferência de nutrientes do ambiente marinho para o terrestre via guano, o que tem importante contribuição para o ciclo do nitrogênio em solos e, enriquecendo-os em nitrogênio e fósforo, contribui para o crescimento de vegetais (Wang et al., 2020). A água de degelo e a precipitação carregam a MO terrígena para o ambiente aquático e promove produção de MO autóctone marinha (Martins et al., 2021).

Dentro desse delicado equilíbrio, a região da Ilha Rei George é climaticamente sensível às mudanças ambientais recentes, e as últimas cinco décadas apresentaram uma taxa de aquecimento de 0,5 a 0,6°C por década (Billups et al., 2021), com um aumento acumulado de 1,0 °C de temperatura de 1948 até 2016 (Pasik et al., 2021).

O Oceano Austral desempenha um papel crucial no clima global da Terra. Ele é um sumidouro significativo de calor e CO_2 e é o oceano mais biologicamente produtivo do mundo (Liu e Curry, 2010). Nas últimas décadas, estudos indicam que ele está passando por mudanças rápidas, apresentando um aquecimento significativo da Corrente Circumpolar Antártica (Gille, 2002, Auger et al. 2021), diminuição de oxigênio (Shepherd et al., 2017) e acidificação (McNeil e Matear, 2008, Henley et al., 2020, Figuerola et al., 2021).

A Península Antártica é a região mais ao norte da Antártica e está localizada no lado oeste do Continente Antártico e tem atraído a atenção da comunidade científica como uma região-chave para estudos sobre mudanças climáticas (Kerr et al., 2018, Henley et al., 2019). Situada em uma zona de transição entre regiões subpolares e polares, ela possui um conjunto de ambientes marinhos únicos sob a influência de processos oceânicos distintos e estressores climáticos, abrangendo o Estreito de Bransfield (Martins et al., 2021).

Algumas das mudanças mais significativas foram detectadas nessa área, com o recuo de quase 87% das geleiras, sem contar os inúmeros colapsos das plataformas de gelo

(Cook et al., 2016). O Oceano Austral conecta a circulação oceânica global e, assim, desempenha um papel chave nos ciclos biogeoquímicos e nas trocas de propriedades entre os compartimentos do sistema terrestre e bacias oceânicas (Orselli et al., 2022).

Para entender as mudanças climáticas que influenciam diretamente a região, é essencial entender as mudanças ambientais mais recentes. Testemunhos de sedimentos marinhos de fiordes na Antártica são apropriados para estudos de flutuações de menor escala de tempo do paleoclima. No entanto, esse tipo de estudo é raro por conta da complexidade da sedimentação glaciomarinha e a disponibilidade limitada de material adequado proveniente dos testemunhos (Yoon et al., 2000).

O ambiente antártico está inserido em uma região importante para o clima terrestre por sua contribuição na captura de CO_2 e a inserção deste na circulação global graças à formação de massas d'águas profundas nesta região. Além disso, o conhecimento sobre a ciclagem do nitrogênio também é ainda insuficiente. Embora longe das atividades humanas, os ecossistemas antárticos são sensíveis às mudanças climáticas globais e às atividades humanas, tornando relevante o estudo do ciclo de nutrientes nessa área (Wang et al., 2020).

A compreensão do ciclo do carbono natural e antrópico no ambiente antártico se enquadra no plano de ação (2023–2032) para a Antártica, que destaca a importância de investigações dos processos biogeoquímicos frente às mudanças ambientais locais e que possam ter impacto nos climas do Brasil e do Atlântico Sul (MCTI, 2023). Além disso, também é relevante no contexto da Agenda 2030 das Nações Unidas, principalmente dentro dos Objetivos do Desenvolvimento Sustentável (ODS) no 13, relativo à tomar medidas urgentes para combater as mudanças climáticas e seus impactos; e no 14, que determina a conservação e uso sustentável dos oceanos, dos mares e dos recursos marinhos para o desenvolvimento sustentável (UN, 2015).

Dessa forma, é válido ressaltar que o trabalho se enquadra como contribuição para a Década da Ciência Oceânica das Nações Unidas, que tem como objetivo propor soluções transformadoras da ciência dos oceanos para o desenvolvimento sustentável. Especialmente, o estudo colabora com o desafio 1: entender e vencer a poluição marinha, com o intuito de compreender e mapear fontes terrestres e marítimas de poluentes e contaminantes e seus potenciais impactos na saúde humana e nos ecossistemas oceânicos e desenvolver soluções para removê-los ou mitigá-los (Década da Ciência Oceânica Brasil, 2020).

O Tratado Antártico (assinado em 1959) e o Protocolo do Tratado Antártico sobre Proteção ao Meio Ambiente (assinado em 1998) estabelecem que todas as atividades realizadas na região deverão ser acompanhadas de estudos que permitam entender as mudanças locais frente aos possíveis impactos antrópicos sobre a dinâmica deste ecossistema (*Antarctic Treaty*, 15 de outubro de 1959).

Assim, esta dissertação contribui para a elucidação das múltiplas faces do carbono orgânico e nitrogênio total sedimentar no sistema antártico e às conexões com mudanças ambientais na hidrosfera marinha antártica e a porção continental adjacente.

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2. Objetivos

2.1 Objetivo geral

Realizar a caracterização elementar e isotópica de sedimentos marinhos de diferentes regiões da Baía do Almirantado, Ilha Rei George, Antártica, a fim de avaliar as possíveis fontes de matéria orgânica para a região.

2.2 Objetivos específicos e hipóteses

- Determinar o conteúdo de carbono orgânico total e nitrogênio total em amostras de sedimentos superficiais e testemunhos coletados na Baía do Almirantado, Antártica.
- Determinar as razões isotópicas do carbono ($\delta^{13}C$) e nitrogênio ($\delta^{15}N$) em amostras de sedimentos superficiais e testemunhos coletados na Baía do Almirantado, Antártica.
- Avaliar a variabilidade espacial e temporal recente dos *mulltiproxy* listados acima frente às diferentes condicionantes ambientais que atuam no ciclo biogeoquímico do carbono e nitrogênio sedimentar local.

As hipóteses que foram testadas são:

1. Se diferentes assinaturas isotópicas do carbono e nitrogênio podem ser relacionadas a fontes naturais da matéria orgânica sedimentar, a variabilidade nos valores destes indicadores geoquímicos em escala espacial e temporal deve refletir as mudanças ambientais associadas à mudança climática local.
2. Se as três enseadas da Baía do Almirantado apresentam características biogeoquímicas diferentes, as fontes da matéria orgânica sedimentar serão distintas.

3. Manuscrito

Fontes de matéria orgânica sedimentar em uma área da Antártica marítima baseada na composição elementar e isotópica: percepções sobre mudanças ambientais locais

A one-century overview of organic matter inputs in sediments of a maritime Antarctica area based on bulk parameters and stable isotopes: insights of local environmental changes

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Abstract

The elemental composition and stable isotopes in the sedimentary organic matter (OM) are important geochemical tools for understanding environments, physical and biogeochemical processes, and even paleoclimatic conditions on Earth. Once the Antarctic Peninsula region is one of the few relatively preserved areas on the planet, sensitive to climate change, and yet remains the most unexplored continent, this study aimed to characterize the elemental and isotopic composition of marine sediments from different regions of Admiralty Bay, King George Island, Antarctica, to assess potential sources of OM. The sampling included: (i) 17 surficial sediment samples collected across the bay in January 2020; (ii) Surficial samples sampled during the 2009–2019 period at three specific sites (one in Ezcurra inlet, another in Mackelar inlet, and the last one in Martel inlet), and; (iii) three sediment cores collected from each inlet of the bay in 2007-2008. A Thermo-Finnigan IRMS Delta V Plus elemental analyzer was applied to determine stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopes, total organic carbon (TOC), and total nitrogen (TN). Grain size analyses used a Malvern Hydro 2000 laser after removing carbonates and OM. OM in sediments from Ezcurra inlet primarily originates from terrestrial plants prevalent in Antarctica, such as mosses, lichens, and aquatic ones. Similarly, the Mackelar inlet is highlighted by significant contributions from these two abovementioned sources and algae. In contrast, Martel inlet exhibits diverse sources, predominantly influenced by various marine mammals and seabirds and their excrements, incorporating signals from mosses and lichens. However, recent sediments sampled post-2008 in Martel inlet show a decreased contribution of animal sources, and mosses and lichens emerging as the predominant sources corroborate patterns observed in the other inlets. The findings of this study provide unprecedented information about the input of OM to sediments in Admiralty Bay, indicating changes over the time scale studied.

Key-words: Sediment core. Surficial sediments. Stable carbon isotope. Stable nitrogen isotope. Admiralty Bay.

Highlights

- Sedimentary organic matter in Admiralty Bay exhibits variation among individual inlets.
- Stable isotopic analysis reveals moss, lichen, and algae prevalent throughout most Admiralty Bay sites.
- A higher contribution of animal-derived organic matter has been noticed in Martel inlet sediments over the last decades.

3.1 Introduction

The Antarctic Peninsula region is considered one of the few relatively preserved areas on the planet, being highly sensitive to climate change and assigned as the most unexplored continent on Earth (Carrizo et al., 2019). It is the northernmost region of Antarctica, located on the west side of the Antarctic continent, and it has attracted scientific attention as a key area for climate change studies (e.g., Kerr et al., 2018; Henley et al., 2019). Located in a transitional zone between subpolar and polar regions, it encompasses unique marine environments influenced by distinct oceanic processes and climate stressors (Martins et al., 2021).

Antarctica serves as a unique natural laboratory for environmental studies, and the Southern Ocean plays a crucial role in the Earth's global climate, acting as a significant sink for heat and CO_2, ranking as the world's most biologically productive ocean (Liu and Curry, 2010). Recent studies indicate rapid changes in the Southern Ocean, including substantial warming of the Antarctic Circumpolar Current, freshening, oxygen reduction, and acidification (Shepherd et al., 2017; Swart et al., 2018; Henley et al., 2020; Auger et al., 2021; Figuerola et al., 2021).

Elemental composition and stable isotopes are essential geochemical tools for understanding environments, physical and biogeochemical processes, and paleoclimatic conditions on Earth (Liu et al., 2022). These tools track the cycling of chemical elements and organic matter (OM) in different planetary compartments, food chain energy flows, nutrient pathways in ecosystems, and changes in the sources of OM to the sediments over various time scales (Corbett et al., 2015), particularly in association with the marine and terrigenous OM cycle (Carrizo et al., 2019).

However, isotopic ratios in Antarctica significantly differ from those found in other places of the world. Galimov (2000) analyzed plant samples from various locations, including the South Shetland Islands, finding different $\delta^{13}C$ values for Antarctic lichens and mosses than those described for tropical and temperate regions.

A considerable number of studies on stable isotopes in maritime Antarctica have covered foraminifera (Yoon et al., 2000; Billups et al., 2021), soil, moss and aquatic microbial mat (Liu et al., 2006, Galimov, 2000, Wang et al., 2000), even in diatoms (Bae et al., 2021) or in adjacent environments, such as lakes on the Antarctic Peninsula (Carrizo et al., 2019). However, few studies use stable carbon and nitrogen isotopes as tracers of sedimentary OM in marine sediments of the Antarctic Peninsula.

King George Island is in the Bransfield Strait as part of the South Shetland Islands (Gheller and Corbisier, 2022). Admiralty Bay, the largest bay on King George Island, is a central location for multiple research stations operated by Brazil, Poland, and Peru.

In Admiralty Bay, studies have described the sources of OM using other geochemical indicators such as iron (Sierpinski et al., 2023), organic markers as isoGDGTs (Dauner et al., 2021), sterols (Wisnieski et al., 2014), and aliphatic hydrocarbons (Martins et al., 2021). Those studies show that molecular composition suggests a mixture of aquatic and terrestrial sources of organic carbon in surface sediments, influenced by aquatic macrophytes, mosses, and lichens, and varying between terrestrial and marine dominance depending on the inlet and season.

This accumulated knowledge about OM dynamics in this region enhances our understanding of local climate, flora, and fauna. The bay remains climatically sensitive to recent environmental changes, with a variable warming rate of 0.5 to 0.6°C per decade over the last five decades and an accumulated temperature increase of 1.0°C from 1948 to 2016 (Billups et al., 2021). Although there has been progress in understanding polar systems over the past decade, significant gaps persist, particularly regarding the processes and patterns in the distribution and source of sedimentary OM in glaciomarine environments. As a result, numerous valuable aspects remain unresolved (Martins et al., 2021).

Therefore, this study aimed to explore the elementary and isotopic signatures of OM from marine sediments collected in Admiralty Bay, King George Island, Antarctica. The sediments analyzed cover a depositional history of one century. They may lead to reconstructing the composition of sedimentary OM from various sources in a period of environmental changes due to the increase of global temperature and local human activities. We hypothesized the environmental changes in the studied area may result in variations in the composition of sedimentary OM along the cores and surficial sediments over time, reflecting the increase of allochthonous OM input from ice-free land areas and the changes in autochthonous OM production.

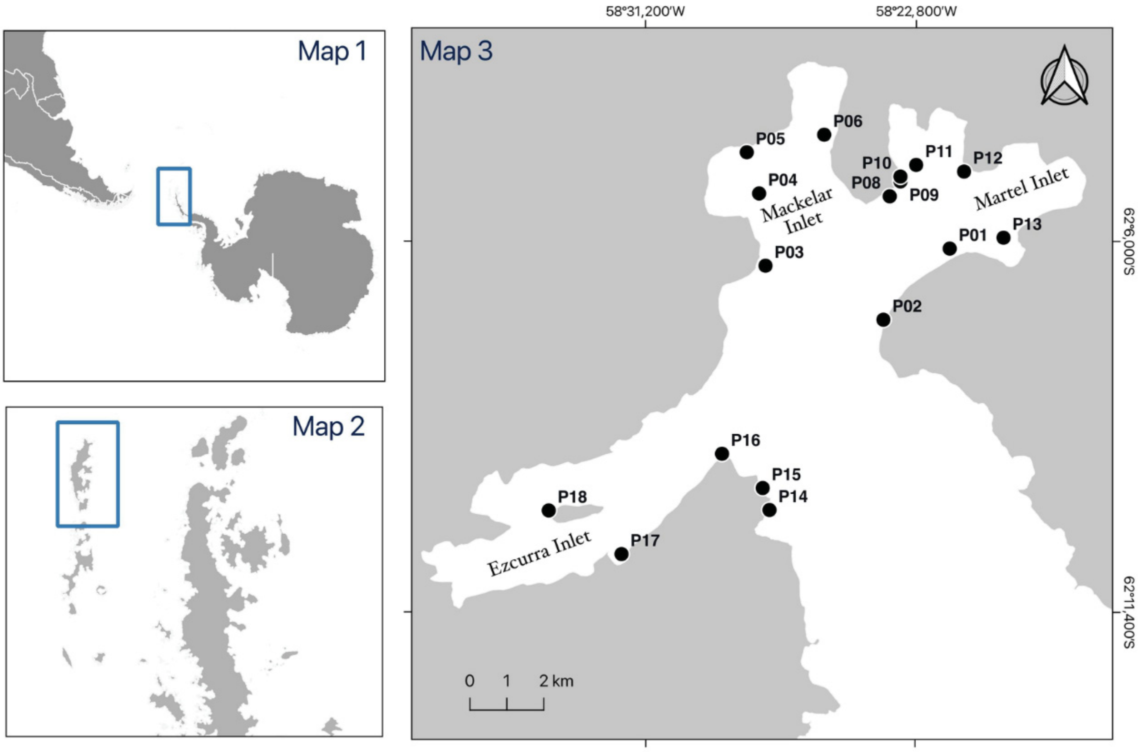
3.2 Study area

Admiralty Bay is a fjord-like polar ecosystem placed on King George Island (62°05’S, 58°23’W), the largest island of the South Shetlands Archipelago, located in the northern part of the Antarctic Peninsula, between the Drake Passage and the Bransfield Strait (Arigony et al., 2002).

This bay has a coastline with several branches divided into three main inlets with a research station in each (Fig. 1): (i) the Brazilian ‘Comandante Ferraz’ Antarctic station (EACF) located in Martel inlet; (ii) the Peruvian ‘Machu Picchu’ station established in Mackelar inlet, and; (iii) the Polish ‘Henry Arctowski’ station, placed in Ezcurra inlet (Cipro et al., 2011).

Precipitation on King George Island exhibits substantial annual variability, with an estimated mean of 701.3 mm from 1968 to 2011 (Kejna et al., 2013). The average annual air temperature oscillates around -1.5 °C, with January being the warmest month (2.4 °C) and June being the coldest (-5.6 °C) based on 2012 observations by Sobota et al. (2015). Comin and Justino (2017) further indicated a temperature increase of 0.8–1.0 °C in the air from 1955 to 2010.

The ocean floor of the bay is 30% dominated by macroalgae (Yoon et al., 2000) and has predominantly coarse sediments coming from the coast. Still, the sediments are a combination of mud and sand as the depth increases (Dauner et al., 2021). Surface sediments exhibit heterogeneity, featuring predominantly coarse sediments such as gravel and sand, primarily located in the outer and central regions of the bay (Fávaro et al., 2011). Ezcurra and Mackelar inlets show a notable variation in grain size distribution, with sand content ranging from 6 to 60%. Conversely, sediments in Martel Inlet consist predominantly of silt and clay fractions, with proportions exceeding 70% (Martins et al., 2005; Berbel and Braga, 2014).



Ezcurra Inlet	**Mackelar Inlet**	**Martel Inlet**	
P14 Llano Point	**P03** Furmanczyk Point	**P01** Botany Point	**P10** Ferraz station II
P15 Arctowski station	**P04** Machu Picchu station	**P02** Hennequin Point	**P11** Steinhouse Point
P16 Thomas Point	**P05** Mackelar	**P08** Refuge I	**P12** Ulmann Point
P17 Monsimet Cove	**P06** Refuge II	**P09** Ferraz station	**P13** Finger Point
P18 Barrel Point			

Fig. 1. Map of the study area showing the Antarctic Peninsula (Map 01), South Shetland Islands (Map 02), and surficial sediment sampling locations in the Admiralty Bay (Map 03).

The scenario of physicochemical properties of the water column in Admiralty Bay was described by Sierpinski et al. (2023), and the water surface had its highest temperature in the Monsiment Cove (P17 in Fig. 1) region, within the Ezcurra inlet, with 5.6°C. In 2020, in the austral summer of surficial sediments sampling, the Antarctic Peninsula experienced its highest recorded air temperature, reaching 20.8°C (Turner et al., 2020; Wachter et al., 2020). Therefore, the results of surficial sediments collected in 2020 may reflect a warmer period on King George Island.

There are areas of special importance for birds and marine mammals on land, and the interaction between the mineral substrate and the mineralization of bird debris generates ornithogenic soils (Soares et al., 2023). In the austral summer, ice-free areas are abundantly vegetated by lower plants such as grasses, lichens, and mosses (Silva et al., 2022). The high carbon, nitrogen, and phosphorus values characterize these soils as important sinks of these elements in terrestrial ecosystems in Antarctica (Dauner et al., 2021).

Admiralty Bay was designated Antarctic Specially Managed Area (ASMA nº.1) during the 1996 Antarctic Treaty System Consultative Meeting (ATCM XXVIII, 2005). This designation, as outlined by Measures in the Protocol on Environmental Protection to the Antarctic Treaty (PEPAT) Annex V, is instrumental in effectively overseeing and managing the impacts of various nations' activities in the region (Montone et al., 2013; Santos, 2022).

3.3 Material and Methods

3.3.1 Sediment sampling

We investigated the parameters: TOC, TN, $\delta^{13}C$, $\delta^{15}N$, carbonates and grain size. Those geochemical proxies were analyzed in the recent spatial scenario, considering: (i) samples collected in the austral summer of 2020; (ii) short temporal variability based on surficial samples collected between the austral summer of 2013 to 2019, and; (iii) three short sediment cores that comprehend the last century.

Surface sediment samples (0–2 cm) were collected at 17 sites in the three different sectors of Admiralty Bay (Martel, Mackelar, and Ezcurra inlets) during the XXXVIII Brazilian Antarctic Expedition, between January and February 2020 (Table S1, as 'S' denotes Supplementary Material), and in three different sites (one site by inlet) spread between austral summer of 2008 and 2019 (Table S2). Sediments were collected using a Van Veen stainless steel bottom sampler, frozen immediately after the sampling, freeze-dried, and homogenized before analysis. The sediments were obtained from a water depth of 20–30 m.

Three sediment cores (one for each inlet), previously described and analyzed by Wisnieski et al. (2014) and Martins et al. (2021), were also considered in this study. These short sediment cores (lengths ranging from 15 to 32 cm) were taken during the austral summer of 2006/2007 using a mini-box core sampler (25x25x55 cm) (Table S3). Cores were subsampled to at least a 2 cm section, placed in aluminium containers, and stored at -20 °C for further analysis (Ceschim et al., 2016).

3.3.2 Core geochronology

For the sediment cores estimated dating, we used the sedimentation rate values obtained in preview studies and presented by Martins et al. (2010 and 2014) (Table S3).

Briefly, the activities of ^{210}Pb and ^{137}Cs were measured by gamma-ray spectrometry EG&G ORTEC, model GMX25190P with photopic of 47 and 661.6 keV, respectively, and resolution from 1.9 to 1332.40 keV. The detailed method (calibration, detector counting efficiency, and errors) was described by Martins et al. (2010 and 2014), and the detector counting efficiency in the photopic region of the radionuclides was evaluated by reference materials from the International Atomic Energy Agency (IAEA), as described by Martins et al. (2015).

Approximate calendar dates were assigned to sediment depths to compare three sediment cores easily and to establish qualitative connections with temporal events in this region. The calculation for the estimated date for each core section was as follows:

$$\textit{Estimated date} = a - (b/c) \qquad \text{(Equation 1)}$$

where: 'a' represented the year when each core was collected (2006 or 2007), 'b' denoted the depth of the core section (in cm), and 'c' corresponded to the estimated linear sedimentation.

3.3.3 Elemental composition and stable isotope analysis

The analytical procedure for the analysis of the carbon (δ^{13}C) and nitrogen (δ^{15}N) isotopic ratios as the percentage of total organic carbon (TOC) and total nitrogen (TN) were based on Mahiques et al. (1999) with minor adaptations.

For the determination of δ^{15}N and the percentage of total nitrogen (TN), about 6 - 8 mg of dry samples were weighed, placed in tin capsules, and measured in an elemental analyser (EA) Costech coupled with an isotopic ratio mass spectrometer (IRMS) Thermo-Finnigan IRMS Delta V Plus. For the determination of δ^{13}C and total organic carbon (TOC), sediments were treated with 2 mL of hydrochloric acid (HCl) (1 mol L^{-1}) to remove inorganic carbon. After that, sediments were repeatedly washed with Milli-Q® water until pH ~7 and dried before being placed in the tin capsules to be measured at the EA-IRMS.

Since the procedure includes the acidification step of the samples to eliminate carbonates from the samples used for $\delta^{13}C$ and TOC, it was possible to use the weight of the samples before and after the application of hydrochloric acid to verify the percentage of carbonate present in the sample.

The analytical accuracy was measured using the USGS-40 (glutamic acid, United States Geological Survey) and IAEA-600 (caffeine, International Atomic Energy Agency) reference standards. The coefficient of variation (e.g., precision), based on the analysis of five replicate samples from Admiralty Bay, ranged from 0.3% for TOC, 0.27% for TN, 0.05‰ for $\delta^{13}C$, 14 for $\delta^{15}N$, and 0.18% for carbonates.

3.3.4 Grain size

Due to limited quantities of sediments available, the grain size analysis was carried out in aliquots of 2 g of surficial sediment only for samples collected during the austral summer of 2020. Decarbonation was performed with a 10% HCl solution, and OM was removed with a 10% hydrogen peroxide (H_2O_2) solution. Each of these components was removed in different steps on a heated plate (65°C for 2 hours).

Grain size was measured in a Malvern Hydro 2000 laser analyzer. The laser is applied to quantify the granulometry of each sample, providing the grain size on the Φ (phi) scale. Samples were sonicated for 5 min before each analysis to avoid flocculation of fine particles. The raw data were processed with the Sysgran 3.2 Software (Camargo, 2006), obtaining the percentages of gravel, sand, silt, and clay for each sample.

3.3.5 Data analysis

Spatial analysis, the studied area map, and maps of the surficial distribution of the studied parameters were generated on the software QGIS (version 3.26).

Statistical analysis was conducted within the R environment (R Core Team, 2018). Boxplots were produced to indicate noteworthy differences among the samples of different inlets and inside each sediment core, considering all the parameters analyzed.

Principal component analysis (PCA) and clustering were performed through the software R Studio. Before the statistical analysis, the variables studied were standardized (raw data were subtracted from the mean value and divided by the standard deviation – z-score padronization). Both approaches determined specific periods in each sediment core that could be divided according to the parameter’s trends.

3.4 Results

3.4.1 The 2020 scenario of sedimentary organic matter in the Admiralty Bay

This section presents the results from all 17 surficial sediments from Admiralty Bay sampled in the austral summer of 2020 (Table S4). The carbonate content ranged from 6.68 (Machu Picchu station, P4) to 22.46% (Ulmann Point, P12), with a mean of 14.66 ± 4.10% (Table S4, Fig. 2a). The lowest median was found in Ezcurra inlet. In contrast, the highest interquartile range (IQR) was verified in Mackelar inlet (Fig. 3a). The percentage of silt+clay presented a mean of 46.66 ± 28.58%, varying from 5.39 (Llano Point, P14) to 97.03% (Barrel Point, P18) (Table S4, Fig. 2b). Sites from Mackelar inlet presented the highest percentage of fine sediments. In contrast, the Ezcurra inlet has the lowest percentage, but there is an outlier (which we adopted as a very different value in relation to other data, excluding the possibility of analytical errors due to the quality standards tested) in Barrel Point, where the highest percentage of fine sediments of the whole bay was found (Fig. 3b).

The mean of TOC was 0.437 ± 0.292 %, ranging from 0.092 (Arctowski station, P15) to 0.986 % (Steinhouse glacier, P11) (Table S4, Fig. 2c). The highest values of TOC were found in the Martel inlet. In contrast, the lowest values were in the Ezcurra inlet, with an increased trend among bay well clear by median and IQR values (Fig. 3c).

The TN presented an average value of 0.070 ± 0.052 %, with the highest value of 0.184 % (Ferraz station II, P10) and the lowest of 0.012 % (Machu Picchu station, P4) (Table S4, Fig. 2d). The TN content was quite similar between Ezcurra and Macklear inlets and the highest values were found in Martel inlet as verified by TOC (Fig. 3d).

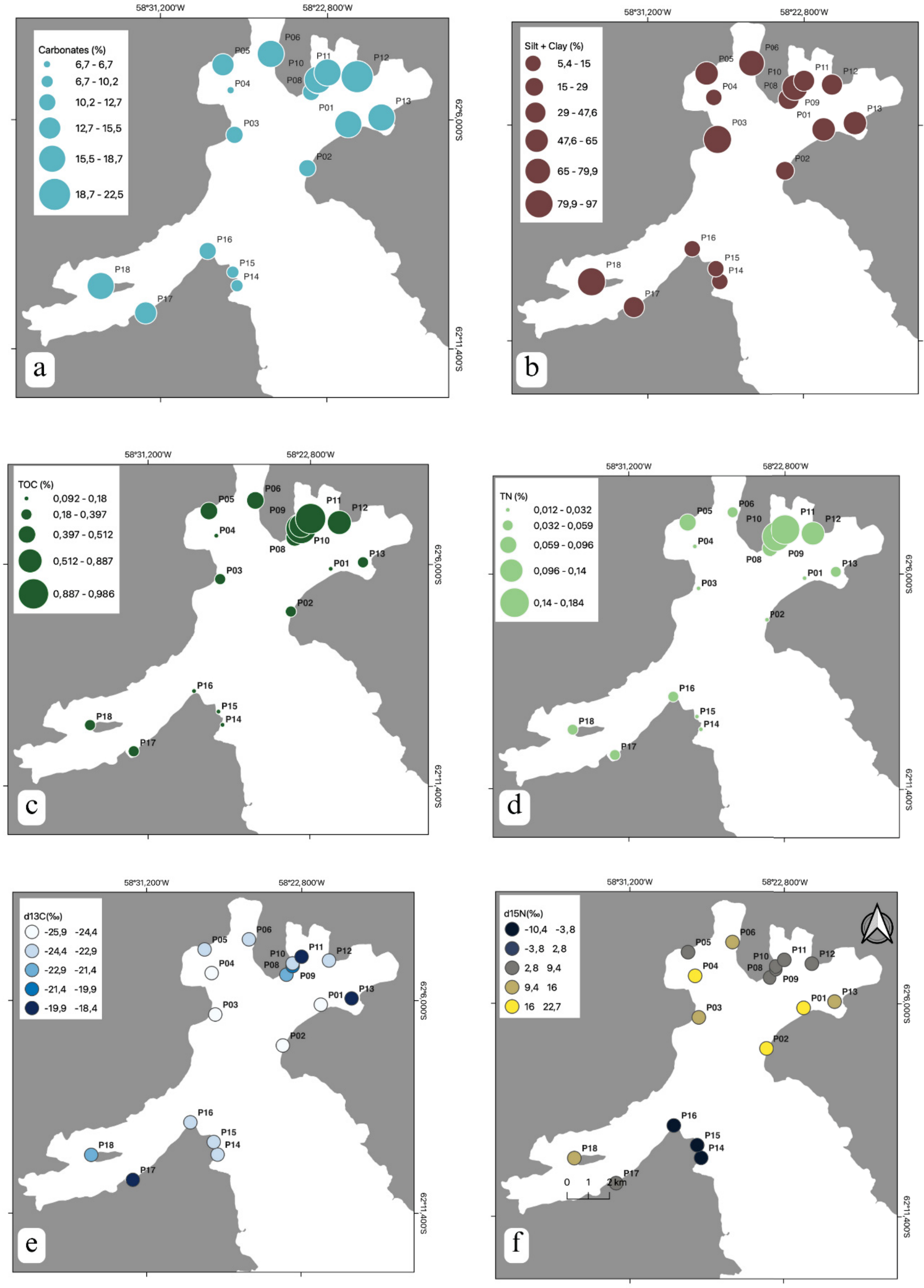


Fig. 2. Spatial distribution of percentage (%) of carbonates (a), silt + clay fraction (b), TOC (c), TN (d), and isotope ratio values of carbon (e) and nitrogen (f) of the surficial sediments of Admiralty Bay sampled in 2020.

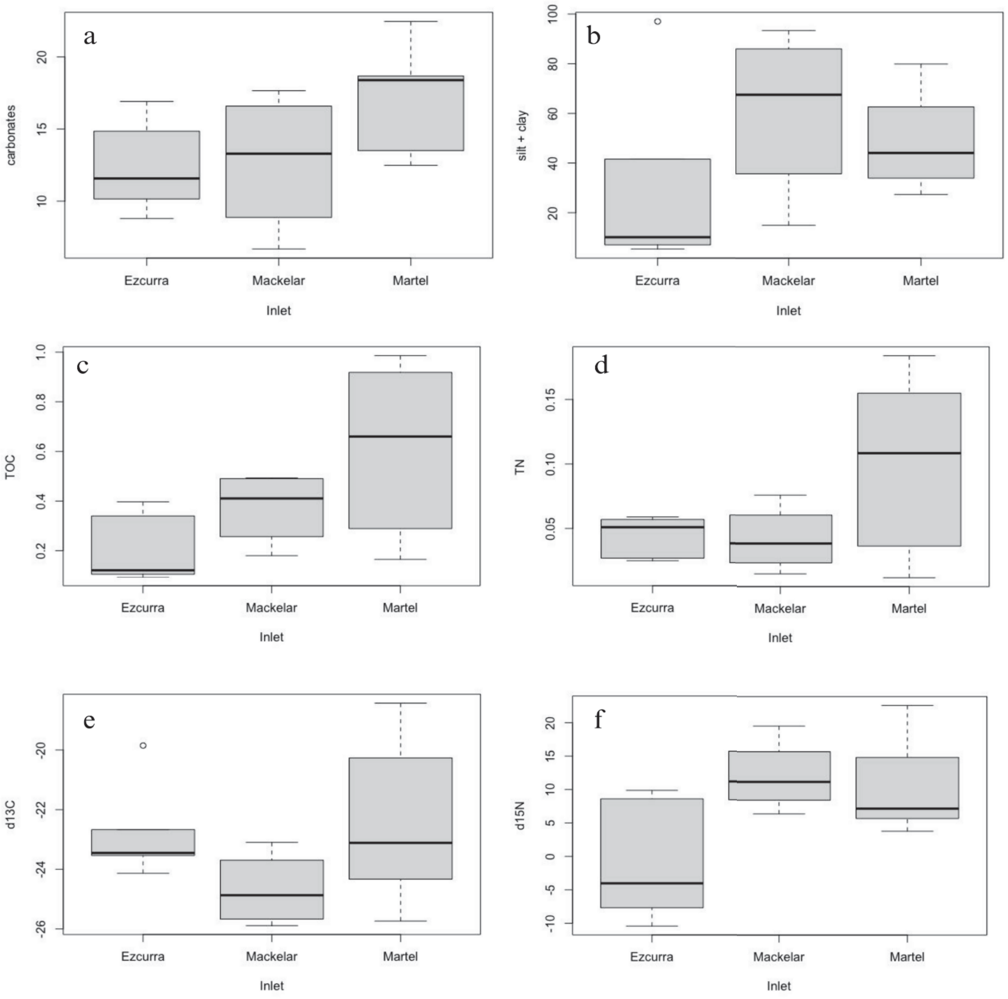


Fig. 3. Boxplots of percentage (%) of carbonates (a), silt + clay fraction (b), TOC (c), TN (d), and isotope ratio value of carbon (e) and nitrogen (f) to the surficial sediments of Admiralty Bay sampled in 2020. The dark line indicates the median.

The lowest value of $\delta^{13}C$ was -25.88‰ (Furmanczyk point, P3), and the highest was -18.42‰ in (Finger point, P13) with a mean value of -23.05 ± 2.14‰ (Table S4, Fig. 2e). A restrict range of $\delta^{13}C$ values was found in Ezcurra inlet. In contrast, values were more variable in the Martel inlet, and the Mackelar inlet presented the relatively lowest values (Fig. 3e).

The $\delta^{15}N$ presented a mean value of 7.46 ± 8.65‰, with a minimum of -10.42‰ (Llano Point, P14) and a maximum of 22.66‰ (Botany Point, P1) (Table S4, Fig. 2f). The $\delta^{15}N$ was quite similar between Martel and Macklear inlets. At the same time, Ezcurra exhibits a more variable range of values and lower values than are found in the other inlets.

The C/N ratio presented a mean value of 8.50 ± 3.70, varying from 2.48 (Thomas Point, P16) to 16.04 (Botany Point, P01) (Table S4, Fig. 4a). In addition, the linear correlation between TOC and TN was calculated and a strong correlation (R = 0.92) was observed, corroborating the application of the atomic C/N ratio as source proxy of sedimentary OM to this group of sediment samples (Meyers, 1997). The boxplot of the C/N ratio shows a variable median among inlets, with lower IQR values in the Ezcurra inlet and higher ones in the Mackelar inlet (Fig. 4b). Also, a strong linear correlation between TOC and TN has been verified, considering the results of these parameters by Martel and Mackelar inlets separately (R = 0.96 and 0.86, respectively), while to Ezcurra inlet, the R = 0.64 (or 0.93, excluding site P16).

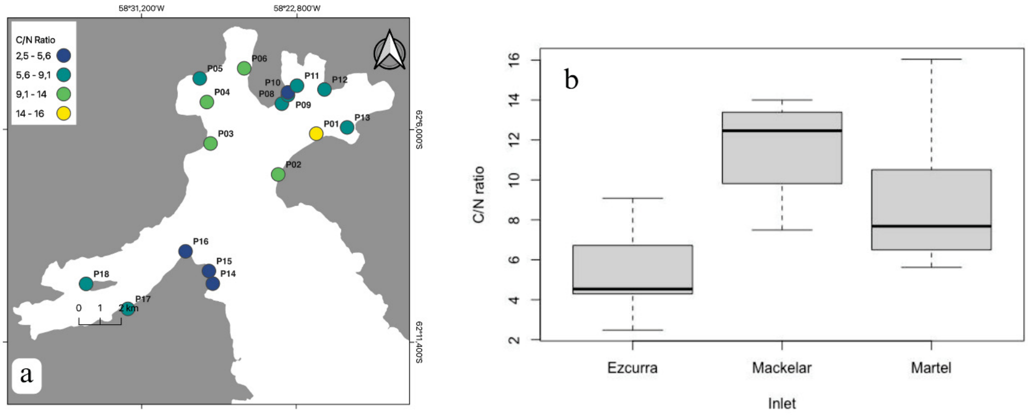


Fig. 6. Spatial distribution (a) and boxplot of C/N ratio to the surficial sediments of Admiralty Bay sampled in 2020, where the dark line indicates the median.

3.4.2 Sedimentary organic matter in samples collected between 2013 and 2020

In this section, we will present the results obtained from surficial sediments collected between the austral summer of 2013 to 2020 at three sites, chosen one in each inlet: i) Ferraz station I, P9, in Martel Inlet; ii) Refuge II, P6, in Mackelar Inlet, and; iii) Barrel point, P18, in Ezcurra Inlet. The parameter values for each year of sampling, as means, maximum, and minimum, are presented in Table S5.

The carbonate content ranged from 12.35 (Bar-S2, 2015, Ezcurra inlet) to 18.49 % (Fer-S1, 2019, Martel inlet) (Table S5). The highest median was found in the Martel inlet, while a similar trend was verified in Mackelar and Ezcurra inlets (Fig. 7).

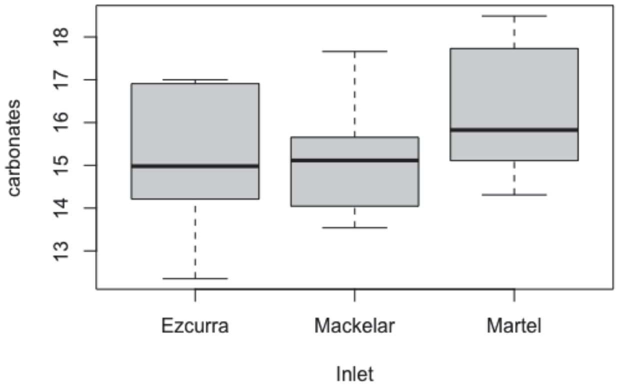


Fig. 7. Boxplot of percentage (%) of carbonates to the surficial sediments of Admiralty Bay sampled between 2013 and 2020. The dark line indicates the median.

The TOC in this period ranged from 0.314 (Bar-S1, 2017, Ezcurra Inlet) to 0.950 % (P9, 2020, Martel inlet) (Table S5). The median values of TOC expressed by the boxplot presented in Fig. 8a were strictly close in the three inlets. The TN ranged from 0.030 (Ref-S7, 2013, Mackelar Inlet) to 0.140 % (P9, 2020, Martel Inlet) (Table S5). The median values of TN were variable among the three inlets, with higher values in the Martel inlet and lower TN content in the Mackelar inlet (Fig. 8b).

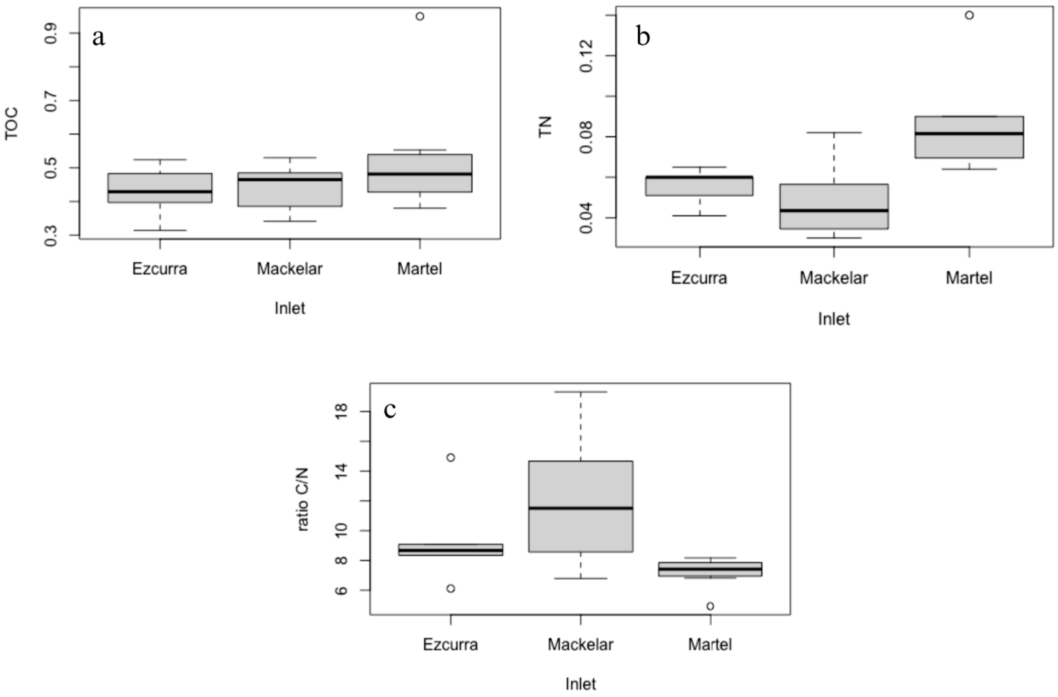


Fig. 8. Boxplots of percentage (%) of TOC (a), TN (b), and C/N ratio (c) to the surficial sediments of Admiralty Bay sampled between 2013 and 2020. The dark line indicates the median.

The C/N ratio varied from 4.93 (Fer-S2, 2014, Martel inlet) to 19.32% (Ref-S4, 2016, Mackelar inlet) (Table S5). The lowest median and low outlier were found in the Martel inlet, which also presents a very low variability in the values of this ratio. The IQR values showed a more variable range of values to Mackelar and Ezcurra inlet, with higher C/N ratio values in Mackelar inlet (Fig. 8c). However, the linear correlation (R) between TOC and TN shown a weak correlation (R = 0.1 - 0.4), limiting the application of the atomic C/N ratio as source proxy of sedimentary OM to these groups of sediment samples (Meyers, 1997).

The $\delta^{13}C$ in this period ranges from -24.73 (Ref-S3, 2017, Mackelar inlet) to -21.33 ‰ (P9, 2020, Martel inlet) (Table S5). The median values of $\delta^{13}C$ expressed by the boxplot presented in Fig. 9a were variable between the three inlets but with lower minimum and maximum values in the Ezcurra Inlet. In comparison, similar values were found in the two inlets remaining inlets to the sites sampled in the austral summer of 2020 (Fig. 9a).

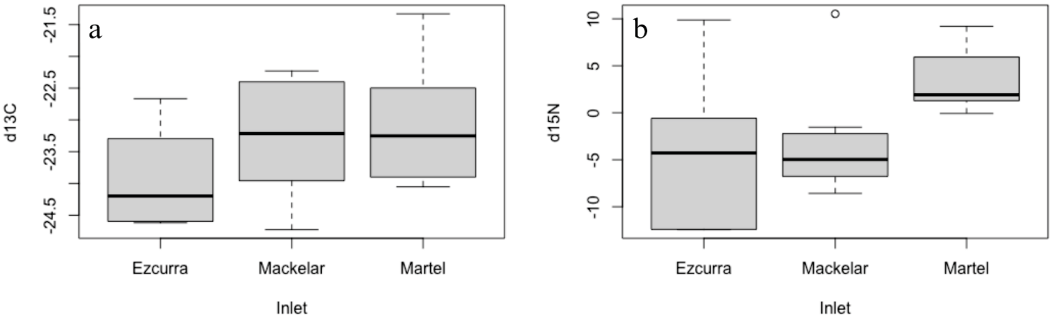


Fig. 9. Boxplots of isotope ratio (‰) value of carbon (a) and nitrogen (b) to the surficial sediments of Admiralty Bay sampled between 2013 and 2020. The dark line indicates the median.

The $\delta^{15}N$ ranges from -12.44 (Bar-S2, 2015, Ezcurra inlet) to 10.53 ‰ (P6, 2020, Mackelar inlet) (Table S5). The negative median values of $\delta^{15}N$ were found at Ezcurra and Mackelar inlets. In contrast, the Martel inlet presented positive values of this parameter (Fig. 9b). The IQR values found in the Mackler and Martel inlets are narrow. In comparison, Ezcurra inlet samples presented a more variable range (Fig. 9b).

3.4.3 Sediment cores results

The results from dated sediment cores collected in the austral summer of 2006/2007 are presented in Table S7.

The median and the interquartile range (IQR) values for carbonate content were lower for sediments from the Ezcurra inlet and higher for the Martel inlet along the period covered by each sediment core per inlet. The minimum and maximum values per each sediment core did not occur in the same period, with lower values detected in 1952 and 1975 in the Mackelar inlet and higher ones in 1964 in the Martel inlet, all of them indicated as outliers in the boxplot (Fig. 10). In general, the carbonate content found in the sediment cores were quite similar to that detected in surficial sediments collected between 2013 and 2020.

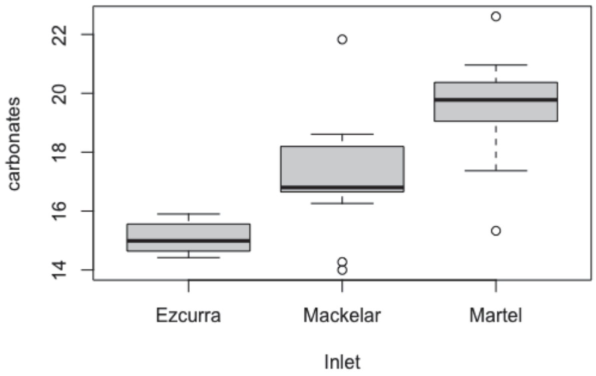


Fig. 10. Boxplots of the percentage of carbonates (in %) to the three sediments cores of Admiralty Bay, Antarctica. The dark line indicates the median.

The boxplots of TOC and TN content present the same trend of median and IQR values, which were lower values to sediments from Ezcurra inlet, similar median to Martel and Mackelar inlets, but more variable range of values to core samples from Mackelar inlet (Fig. 11a and b). The relatively low IQR in Ezcurra and Martel inlets compared to Mackelar indicates the stable content of these elements over the period. In addition, the sediments from the first 4 cm (1998 - 2007) of the Martel inlet core presented the highest concentrations of TOC and TN, shown as outliers and indicative of fresh OM recently deposited (Fig. 11a). Relatively higher values of TN, also indicated as outlier, have been verified in specific sections of the Barrel point core, as Bar-2 (2003), Bar-5 (1991) and Bar-14 (1963) (Fig. 11b).

The low medians of the C/N ratio were found in Mackelar and Martel inlets, which also present a low variability in the values of this ratio. In contrast, the Ezcurra inlet presented a more variable IQR, with a higher C/N ratio, despite the lower value of Bar-T5 (1991) assigned as an outlier (Fig. 11c). The linear correlation (R) between TOC and TN showed a weak correlation (R = 0.26 - 0.44, excluding outliers), similar than surficial sediments between 2013 – 2020, limiting the application of the atomic C/N ratio as source proxy of sedimentary OM (Meyers, 1997).

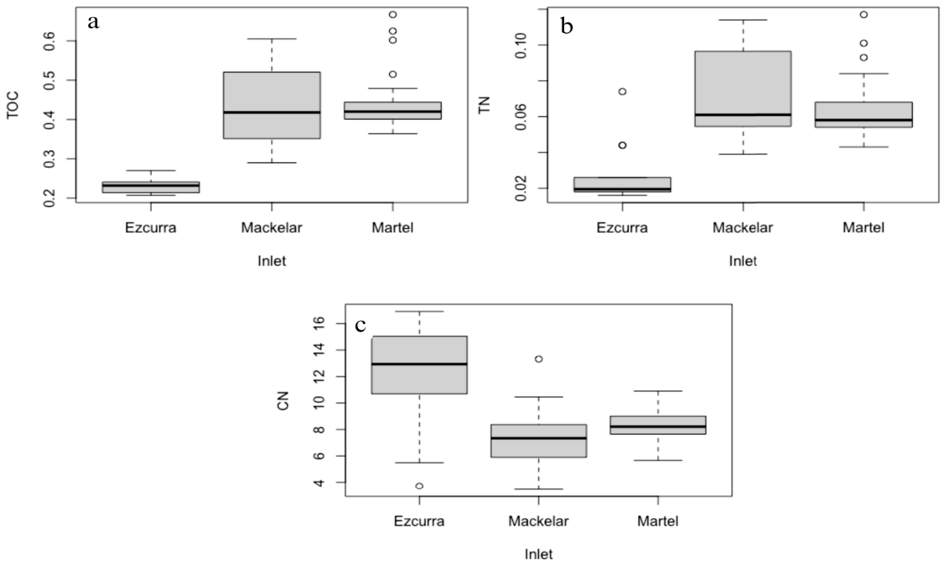


Fig. 11. Boxplots of TOC (%) (a), TN (%) (b), and C/N ratio (c) to the three sediments cores of Admiralty Bay, Antarctica. The dark line indicates the median.

Overall, for the δ^{13}C, Ezcurra and Mackelar inlet cores showed higher IQR and median δ^{13}C values. In contrast, Martel had the lowest ones (Fig. 12a). Maximum values pointed as outliers were not significantly above the upper limit observed in the boxplots (Fig. 12a). The δ^{15}N presented a similar pattern to δ^{13}C, especially between Ezcurra and Mackelar inlets are compared. In contrast, Martel had a different trend, with higher and positive values. Based on the isotopic ratios, Ezcurra and Mackelar inlets are under similar sources of OM over the evaluated period, while Martel seems influenced by different contributions than indicated in the other inlets.

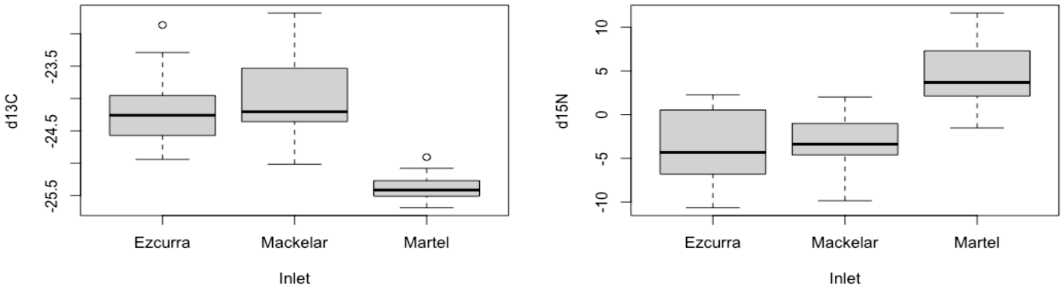


Fig. 12. Boxplots of δ^{13}C (a) and δ^{15}N (b) to the three sediments cores of Admiralty Bay, Antarctica (in ‰). The dark line indicates the median.

3.5 Discussion

3.5.1 Comparative insights considering parameters variations in Admiralty Bay and across Antarctica

Grain size obtained by the sediments collected in 2020 showed an Admiralty Bay seafloor with significant variability in the fine fraction (silt and clay), with distinct variations observed within each specific inlet. Similarly, other studies have found a higher percentage of silt and clay in Martel Inlet (e.g., Yoon et al., 2000; Fávaro et al., 2011; Berbel and Braga, 2014) and a notably heterogeneous sediment coverage (ranging from 6 to 60% of sand fractions) in surface sediments, with coarser sediments particularly prevalent in the central and outermost regions of the bay (Berbel and Braga, 2014).

The sheltered area in Ezcurra inlet, where Barrel point (P18) is located, presented an actual sedimentary composition based on fine fractions related to less wave and current energy (Campos et al., 2012). On the other hand, sites more exposed to currents and waves, i.e., high energy and close to the entrance of the bay, such as P14, P15, P16, and Mackelar inlet, showed a relatively low percentage of fine sediments, TOC, and TN. Then, more exposed areas to the Bransfield Strait may contain less fine sediment content.

This dynamic is also assessed by Freitas et al. (2021), who found the relatively higher total phosphorus concentration observed in the inner section (Barrel Point) compared to the inlet entrance (Thomas Point) of Ezcurra inlet, which may be attributed to variations in grain size distributions. Conversely, Monsimet Cove, located in the mid-sector of the Ezcurra Inlet, experiences a direct influence from ice melting and freshwater runoff originating from a small glacier covering the adjacent land (Schofield et al., 2010; Simms et al., 2011), promoting an increase in terrestrial input and intermediate percentage of fine sediments compared to the abovementioned areas.

Similar patterns are observed in other bays across the Antarctic continent (e.g., Flandres Bay, West Antarctic Peninsula), in which high percentages of fine sediments were found in the inner sectors of bays, indicating that fine-grained deposits from meltwater plumes and sediment gravity flows near the glacier front (Munoz and Wellner, 2016). The middle sector of the bays usually exhibited a high silt percentage, with sediments rich in diatoms. In contrast, the outer sector displayed a substantial contribution of coarse material, assumed to be the outcome of wind and snow currents (Munoz and Wellner, 2016).

The carbonate content found in the surficial sediments of Admiralty Bay, especially Martel inlet, indicates primary production and pronounced marine influence (Hauck et al., 2012). The carbonate range follows the results presented by Franco et al. (2017), who found a carbonate content of 17% in sites close to the Brazilian Antarctic station, while other sites located closer to the main channel of the bay exhibited values ranging from 14 to 19%. Extensive carbonate oozes are typically found only in shallow, low-latitude sediments (e.g., Milliman et al., 2012; Seiter et al., 2004). Carbonate contents in surface sediments are generally low, and elevated ones (>15%) are observed at shallow water depths (150–200 m) of the Southern Ocean (Seiter et al., 2004). The Western Antarctic Peninsula region presents a patchy carbonate standing stock associated with the macrozoobenthic. In contrast, the sedimentary carbonate is uniformly distributed but low compared to other regions (Hauck et al., 2012), consistent with the findings in Admiralty Bay, as values do not exceed >30%.

Sites that are more susceptible to wave and current transport, i.e., open regions of the entrance bay and in Mackelar and Ezcurra inlets, presented lower TOC and TN range values. Conversely, Martel Inlet exhibits higher values of these parameters, especially near the Brazilian Ferraz Station (sites P9 and P10). High levels of TOC and TN may be related to the occurrence of vegetation inland (Putzke et al., 2022).

In addition, seabed macroalgae are abundant and widespread in Admiralty Bay, particularly in Martel inlet (Alcântara et al., 2023), which may contribute to the deposition and accumulation of biogenic material in the inner sectors. However, currents can transport fine biogenic sediments to the Bransfield Strait (Yoon et al., 2000) and/or deposited on the beaches as drifting algae (Colepicolo et al., 2014).

The TN levels were higher in Martel inlet, near the Brazilian Antarctic Station, which could be a potential anthropogenic source of sedimentary OM since previous studies addressed the occurrence of pollutants (e.g., hydrocarbons; Martins et al., 2010), sewage markers (e.g., linear alkylbenzenes and coprostanol; Martins et al. 2002, Montone et al. 2010). Total phosphorus (TP), like nitrogen, has been detected in the vicinity and can be related to wastewater discharged by the Antarctic research station (Freitas et al., 2021). An increased TP indicated by the Phosphorus Pollution Index (PPI $\geq$ 1.3) has been associated with the establishment and operation of sewage treatment facilities that contribute to discharge of nutrients as nitrogen and phosphorus to Martel inlet waters (Freitas et al., 2021). In addition, these elements are crucial nutrients also derived from the weathering of crustal materials and enter the ocean mainly through freshwater runoff and dust deposition (Benitez-Nelson, 2000; Paytan and McLaughlin, 2007).

Also, the increased TN can be associated with the recent deposition of naturally derived OM, particularly near sources of ornithogenic soils or submerged fields of macroalgae, where increased TP has also been verified (Freitas et al., 2021). Petry et al. (2015) described the region near the Brazilian Antarctic station (e.g., sites P1, P8, P9, P10, and P11) as home to several groups of seabirds, including the south polar and brown skuas, kelp gull, and Antarctic tern. This finding supports a natural contribution of the TN to the local sedimentary OM.

Higher TOC and TN levels were also verified in samples from the Mackelar inlet sediment core and may be related to the occurrence of lower tidal currents speed in this inlet (~0.02 m s^{-1}) (Weber and Montone, 2006). The TOC values of Admiralty Bay inlets are not higher than other regions of Antarctica. For instance, Berg et al. (2021) reported surface sediment TOC contents ranging from 0.4 to 0.8% in Cumberland Bay and on the adjacent shelf. Little Jason Lagoon showed levels around 3%, both sites on South Georgia Island. Marine fjords at both high and mid-latitudes, shaped by the influence of terrestrial contributions from rivers and glacial erosion, demonstrate sediment accumulation with varying OM content, contingent upon the characteristics of their catchment areas (Bianchi et al., 2020).

Another contribution to sedimentary OM is the input of marine mammals and birds to the environment, which impacts the proportion between TOC and TN in surface sediments. Soils influenced by penguin droppings exhibit significantly elevated nitrogen concentrations but lower carbon content (i.e., low C/N ratio) than the plant-derived humus (Liu et al., 2006). As vegetation re-establishes itself in deserted rookeries, a rapid rise in the C/N ratio within the ornithogenic OM of relic soils is expected. Moreover, as vegetation undergoes successive stages of succession in an age-related sequence of abandoned nesting sites, the C/N ratios within the relic soils may steadily increase (Liu et al., 2006).

Then, the presence of vegetation leads to increased TOC, consequently resulting in higher C/N ratios. Therefore, samples with higher C/N ratios can be due to the influence of the terrigenous input from this process of succession colonization of the soil.

Penguin colonies near sites P14, P15, and P16 in the Ezcurra inlet were described by Petry et al. (2010; 2016), and those seabird colonies may explain the lower C/N ratio were found in surficial sediments, once the contribution to TN is relatively higher than locations without this type of source. On the other hand, sites with glaciers may also exhibit higher C/N ratios due to the runoff of meltwater providing such contributions.

Particularly for sediments collected in the austral summer of 2020, high temperatures were recorded during this period, increasing the ice melting and, therefore, the terrigenous input (Turner et al., 2020; Wachter et al., 2020). In fact, the sites in Mackelar Inlet are influenced by the Mackelar Glacier, as well as in Martel Inlet, especially at P1, which may be influenced by Krack and Wanda Glaciers (Vieira et al., 2015; Wójcik et al., 2019).

Corroborating this influence, Pichlmaier et al. (2004) found a higher concentration of suspended sediments near glaciers located in Martel Inlet. Taylor et al. (2020) presented C/N ratios in surface samples from the West Antarctic Peninsula shelf, ranging from 8.0 to 9.8 (mean = 8.5). On the other hand, Mincks et al. (2008) found lower values ranging from 6.0 to 7.4 to both surface and subsurface sediments. Our results indicate variable values in the three inlets during the studied periods, sometimes higher and sometimes lower, but with a C/N ratio >10 in Ezcurra Inlet, which is relatively higher than in other different Antarctic regions.

The controlling processes of the C/N ratio and their limited uses as proxy of OM source due to the absence of linear correlation between TOC and TN in surficial sediments from 2013 and 2020 and in the sediment cores drive alert to the importance of a multiproxy approach to a precise evaluation of OM sources in Antarctic sediments.

3.5.2 Environmental changes and sources of organic matter based on stable isotope ratios

The isotopic ratios of $\delta^{13}C$ and $\delta^{15}N$ can be used to determine the sources of OM in marine sediments (Meyers, 1994; Lam, 2006) in a spatial perspective and throughout the entire time covered by sediment cores.

The isotopic ratio values were compared with ranges previously described in studies conducted in Antarctica, as illustrated in Fig. 13. This compilation was first presented by Liu et al. (2006), according to the results provided by several authors (e.g., O'Lary 1988; Chen et al., 1997; Cocks et al., 1998; Liu et al., 1998; Huang et al., 1998; Mizutani and Wada, 1998; Wainright et al., 1998; Galimov, 2000; Kaehler et al., 2000; Li et al., 2002).

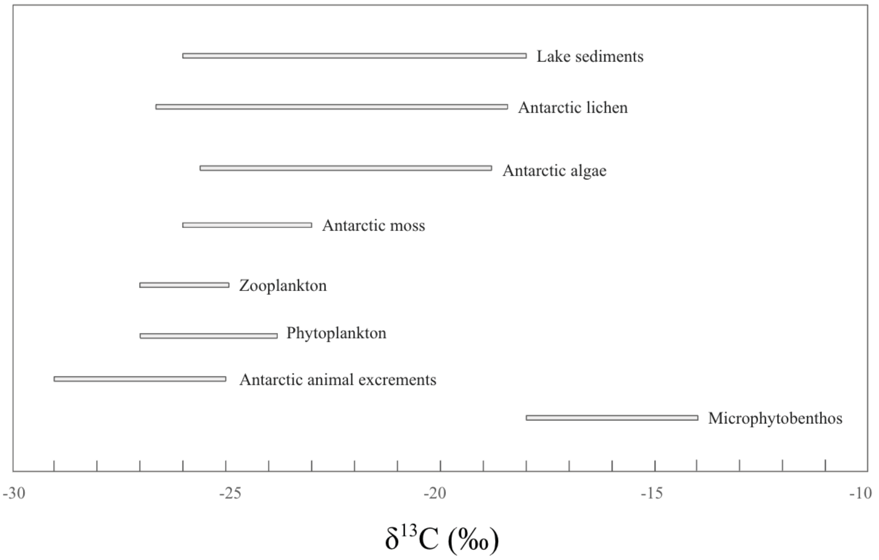


Figure 13. Compilation of $\delta^{13}C$ value ranges of organic matter (OM) from various sources in the Antarctic region, as documented by prior research (Liu et al., 2006 and references therein: Liu et al., 1998; Li et al., 2002; Galimov, 2000; Kaehler et al., 2000) and Corbisier et al., 2004.

According to Fig. 13, the same specific range of $\delta^{13}C$ values may result in different sources of sedimentary OM. Then, a cross plot of $\delta^{13}C$ and $\delta^{15}N$ may help to narrow down the more probable OM source. To achieve this, we also compiled $\delta^{15}N$ data from studies conducted in Antarctica (e.g., Wada et al., 1981; Mizutani and Wada, 1988; Cocks et al., 1998; Wainright et al., 1998; Liu et al., 2006; Cipro et al., 2011; Nie et al., 2014) (Fig. 14).

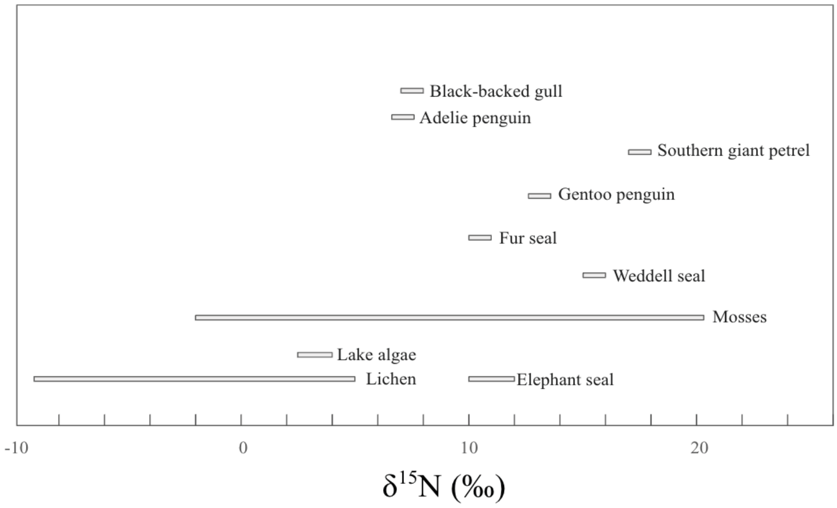


Figure 14. Compilation of $\delta^{15}N$ value ranges of the OM from different origins in the Antarctic region, described by previous studies (Wada et al., 1981; Mizutani and Wada, 1988; Cocks et al., 1998; Wainright et al., 1998; Liu et al., 2006; Cipro et al., 2011; Nie et al., 2014).

Considering the entire temporal series covered by the samples from sediment cores and surficial sediments from 2013 and 2020, the $\delta^{13}C$ values in Ezcurra Inlet were predominantly around -24‰ (Tables S4, S5 and S6, and IQR from Fig. 15a). This suggests a potential association with phytoplankton algae, mosses, lichens, or even material from lake sediments (Fig. 13). Furthermore, the $\delta^{15}N$ values within the inlet primarily range from -8 to 0‰ (Tables S4, S5 and S6, and IQR from Fig. 15b), typically found on lichens and mosses (Fig. 14). Then, these two sources are likely the most prevalent contributors in Ezcurra Inlet.

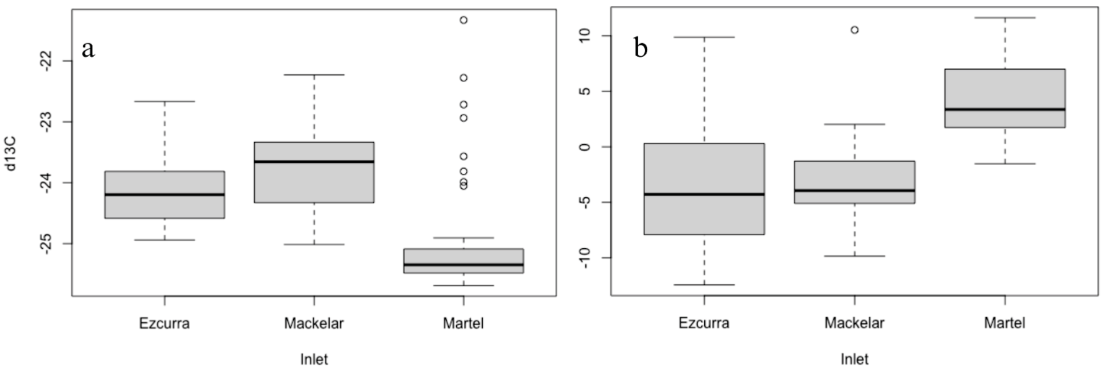


Figure 15. Boxplots of the $\delta^{13}C$ (a) and $\delta^{15}N$ (b) distribution in each inlet, comprising all samples in the temporal series.

Meltwater from glaciers increases the terrigenous input, which contains sediments more depleted in ^{13}C. However, this input of terrigenous material may bring nutrients to the adjacent waters close to the glacier. Bae et al. (2021) studied Marian Cove, located on King George Island. They found relatively higher values of $\delta^{13}C$ in coastal sediments near the glacier, in a similar range than to phytoplankton and diatoms, with a tendency to decrease with the increase of distance from the glacier. Following this trend, the sites from Ezcurra inlet that have shown more enriched with ^{13}C (i.e., higher $\delta^{13}C$) are likely influenced by glaciers, as site P17, located near Dera Icefall (Wójcik et al., 2019).

The Mackelar inlet exhibited some fluctuation in $\delta^{13}C$ values (Tables S4, S5, and S6, and IQR from Fig. 15a). The more ^{13}C enriched samples presented $\delta^{13}C$ values related to material from freshwater lake sediments, phytoplankton, lichens, and algae (Fig. 13). However, most of the samples are in the range of -24.5 to -23.5‰, where moss emerges as an important source. The ^{13}C depleted samples (~ -25‰) in the sediment core suggest an increment to this source, in addition to the influence of zooplankton and animal excrement inputs. On the other hand, the $\delta^{15}N$ pointed to algae, mosses, and lichens along the sediment core. The excrement of marine mammals (such as fur and elephant seals) appears to be more significant only in the surficial sample collected in 2020.

The Martel inlet exhibited significant fluctuation in $\delta^{13}C$ values (Tables S4, S5 and S6, and IQR from Fig. 15a) when surficial and sediments core samples are compared, presenting a unique scenario, where most values reflecting older sediments are within a narrow range, and sediments from 2013 until 2020 appear as outliers (Fig. 15a). Samples from sediment core presented depleted ^{13}C with values between -26 to -25‰, indicating the contribution of phytoplankton, zooplankton, marine animal excrement, lichens, and lake sediments (Fig. 13). As for the surficial sediments, there are eight enriched ^{13}C samples, with values around -23 and -22‰, and the minimum found in the most recent sample collected in 2020 (-21.3‰).

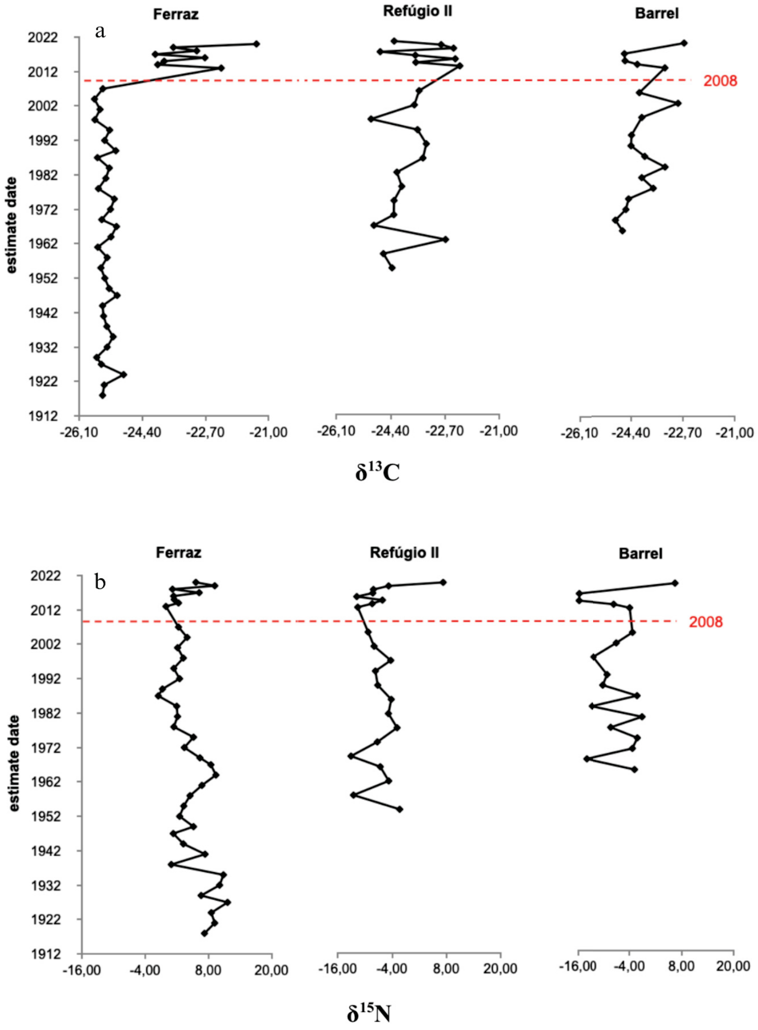


Figure 16. Downcore profiles of $\delta^{13}C$ (a) and $\delta^{15}N$ (b) in sediments from Admiralty Bay. The red line indicates the distinction between surficial sediment samples collected between 2013 and 2020 and sediment core samples collected in 2007 per each inlet.

These results demonstrate that the sources of OM were relatively stable from 1912 to 2008 (expressed by sediment core data) and changed in the sediments sampled from recent years, reflecting less contribution from phytoplankton, zooplankton, and marine animals. Examining the $\delta^{15}N$, this mixture of sources is indeed influenced by animal activity, reflecting signals from both mosses and lichens and the range of marine mammals, such as elephant seals, fur seals, and seabirds, as black-backed gulls, and Adélie penguins (Fig. 14).

Ezcurra and Mackelar Inlets presented similar organic matter sources, while Martel's historical series shows that for the majority of the time, this Inlet experienced distinct influences (Figure 17). The samples most closely resembling the others are from the most recent years, where less negative values are observed between 2013 and 2020, approaching the conditions observed in the other two inlets, with less evidence of phytoplankton, zooplankton, and marine animals.

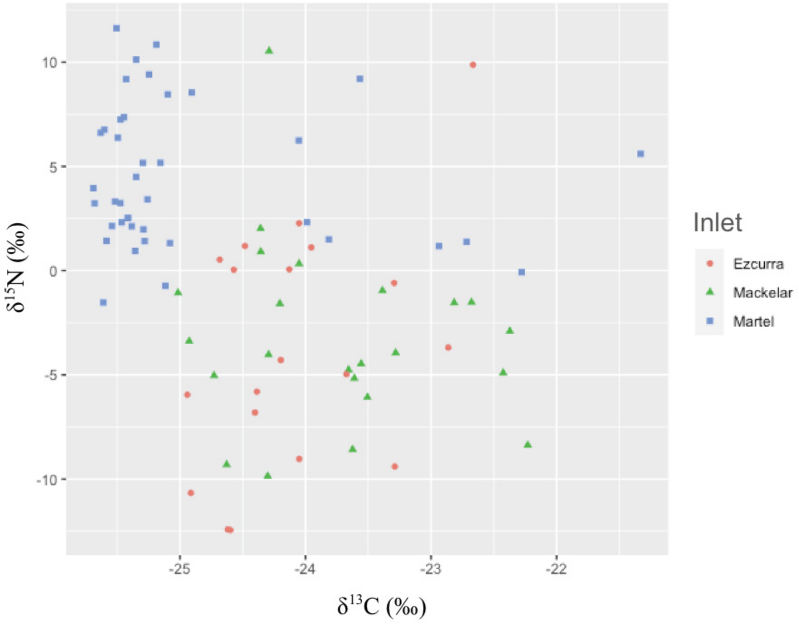


Figure 17. Crossplot of the $\delta^{13}C$ and $\delta^{15}N$ comprising all samples in the temporal series. Different colours and symbols represent the inlets Ezcurra (red circles), Mackelar (green triangles) and Martel (blue squares).

The composition of sedimentary OM in Admiralty Bay based on the stable isotope approach (Fig. 16a and 16b) can be compared with other geochemical parameters determined in the same sediment cores, that indicating terrigenous/continental influence, as TP (Freitas et al., 2021), or marine/aquatic molecular indicators as short-chain *n*-alkanes, biogenic sterols (e.g., dinosterol), and aquatic *n*-alkane proxy (P_{aq}) (Martins et al., 2014, 2021; Wisnieski et al., 2014). Based on these findings, the marine influence in the 'older' samples appears on each sediment core. For instance, in Ezcurra inlet, a distinct contribution of short-chain *n*-alkanes, dinosterol, and cholesterol (a sterol related to phyto- and zooplankton) is clear in bottom sections of the core (Wisnieski et al., 2014; Martins et al., 2021). The Mackelar inlet core exhibited highly variable values of the abovementioned parameters and revealed a more terrigenous signal near top core sections (1985 to 2008). A similar pattern was found in the Martel inlet sediment core, with a higher terrigenous contribution in the medium-top core and a more marine influence at the bottom sections (Wisnieski et al., 2014; Martins et al., 2021).

However, some trends verified by molecular indicators were not clear based on $\delta^{13}C$ and $\delta^{15}N$ analyses, which makes it difficult to establish a direct correlation between the Martel inlet core isotope data and the sea surficial temperature (SST) variations as observed by Dauner et al. (2021), which demonstrated an increased trend on SST in a sediment core collected at Botany Point, also located in the Martel inlet.

3.6 Conclusions

The current study was designed to provide the first information about the distribution of stable isotope and C/N ratios and their application as sedimentary OM tracers in Admiralty Bay, Antarctica. It contributes to the comprehension of biogeochemical interactions that influence the supply of OM to sediments, laying the groundwork to evaluate future changes in this highly vulnerable system in the face of climate change.

The comprehensive analysis of bulk-element, grain size, and carbonate in the recent scenario enabled us to assess the distribution of these parameters in the region and establish correlations with the specific characteristics of each inlet. This approach aimed to unravel the complexity of the scenario in Admiralty Bay by considering all relevant parameters.

Sediment cores provided a temporal series of isotopes and elementary data per each inlet, offering insights into the historical deposition of OM spanning the past century. Our results unveil various potential OM sources for sediments of Admiralty Bay, and each inlet possesses a distinct depositional record.

In summary, the primary sources of OM in sediments of Admiralty Bay appear to originate from terrestrial and aquatic plants prevalent in Antarctica, such as mosses and lichens, with specific secondary sources according to each inlet. The Mackelar and Ezcurra inlet sites presented significant contributions of these two abovementioned sources, accompanied by algae. Martel inlet displays a diversity of sources predominantly influenced by animal activity, represented by marine mammals like elephant seals, fur seals, and seabirds such as black-backed gulls and Adélie penguins in recent times. However, since 2013, the surficial sediments reflected a decreased influence of animal activity, with mosses and lichens emerging as the predominant sources, aligning with the patterns observed in the other inlets.

There is still a substantial lack of studies addressing specifically the stable isotopes as indicators of the sedimentary OM origin in marine sediments in Antarctica, which limits the comparison between polar marine environments. It is evident that further research is essential to enhance our understanding of stable isotopes as proxies of environmental changes and their implications.

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3.8 CRediT authorship contribution statement

Viviane K. Bisch: Conceptualization, Formal analysis, Writing – original draft, review & editing, Visualization. Satie Taniguchi: Formal analysis, Writing – review & editing. Rafael André Lourenço: Writing – review & editing. Márcia C. Bícego: Resources, Writing – review & editing. Rosalinda C. Montone: Resources, Writing – review & editing; César C. Martins: Conceptualization, Formal supervision, Resources, Writing – review & editing, Funding acquisition, Project administration.

3.9 Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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4. Considerações Finais

A análise das assinaturas isotópicas do carbono e nitrogênio revelou que a variação espacial e temporal das fontes naturais da matéria orgânica sedimentar pode refletir as mudanças ambientais decorrentes da mudança climática local, principalmente nas últimas duas décadas. Além disso, foi identificada uma distinta variação biogeoquímica entre as três enseadas da Baía do Almirantado, confirmando a hipótese de diferentes fontes de matéria orgânica sedimentar em cada uma delas.

Este estudo contribui significativamente para a compreensão das interações biogeoquímicas que influenciam o suprimento de matéria orgânica aos sedimentos na região da Baía do Almirantado, na Antártica. Ao considerar diferentes *proxies*, desde elementos em massa até características específicas de cada enseada, foi possível observar a complexidade do cenário local e estabelecer correlações importantes. Além disso, a análise de testemunhos sedimentares proporcionou uma visão temporal da deposição de matéria orgânica ao longo do último século, revelando múltiplas fontes potenciais de matéria orgânica para os sedimentos da região.

Esses resultados não apenas respondem às hipóteses levantadas, mas também têm implicações significativas para a compreensão da vulnerabilidade desse ecossistema polar frente às mudanças climáticas em curso. Ao ampliar nosso conhecimento sobre a dinâmica biogeoquímica da Baía do Almirantado, este estudo estabelece uma base sólida para investigações futuras sobre as respostas dos sistemas costeiros antárticos às alterações ambientais globais.

5. Anexo

Table S1. Surficial sediment sampling sites collected in austral summer of 2020 in Admiralty Bay, King George Island.

Code	**Sampling site name**	**LAT (S)**	**LONG (W)**	**Distance to the coast (m)**
P1	Botany point	62°06.110'	58°21.750'	250
P2	Hennequin point	62°07.147'	58°23.806'	45
P3	Furmanczyk point	62°06.363'	58°27.473'	250
P4	Machu Picchu station	62°05.311'	58°27.672'	705
P5	Mackelar glacier	62°04.712'	58°28.056'	100
P6	Refuge II	62°04.455'	58°25.654'	290
P8	Refuge I	62°05.350'	58°23.617'	130
P9	Ferraz station I	62°05.133'	58°23.286'	50
P10	Ferraz station II	62°05.063'	58°23.286'	50
P11	Steinhouse point	62°04.893'	58°22.798'	470
P12	Ulmann point	62°04.988'	58°21.311'	135
P13	Finger point	62°05.949'	58°20.080'	380
P14	Llano point	62°09.920'	58°27.343'	70
P15	Arctowski station	62°09.600'	58°27.554'	100
P16	Thomas point	62°09.102'	58°28.822'	100
P17	Monsimet cove	62°10.562'	58°31.951'	205
P18	Barrel point	62°09.926'	58°34.216'	95

Table S2. Surficial sediment sampling sites collected between in austral summer of 2013 and 2020 in Admiralty Bay, King George Island.

Code	Sampling site name	LAT (S)	LONG (W)	Sampling year
P6	Refuge II	62°04’27”	58°25’39”	2020
Ref-S1		62°05’11”	58°25’48”	2019
Ref-S2		62°04’25”	58°25’22”	2018
Ref-S3		62°04’22”	58°25’20”	2017
Ref-S4		62°04’24”	58°25’20”	2016
Ref-S5		62º04’26”	58º25’25”	2015
Ref-S6		62º04’26”	58º25’25”	2014
Ref-S7		62˚05’11”	58°25’48”	2013
P9	Ferraz station I	62°05’08”	58°23’17”	2020
Fer-S1		62°05’09”	58°23’03”	2019
Fer-S2		62°05’08”	58°23’18”	2018
Fer-S3		62°05’07”	58°23’07”	2017
Fer-S4		62°05’07”	58°23’18”	2016
Fer-S5		62º05’08”	58º23’11”	2015
Fer-S6		62º05’08”	58º23’11”	2014
Fer-S7		62º05’12”	58º23’10”	2013
P18	Barrel point	62°09’56”	58°34’13”	2020
Bar-S1		62°10’04”	58°32’50”	2017
Bar-S2		62°10’16”	58°35’30”	2015
Bar-S3		62º10’21”	58º31’28”	2014
Bar-S4		62º10’21”	58º31’28”	2013

Table S3. General information of sediment cores collected at Admiralty Bay, King George Island, Antarctica.

Core name	**Inlet**	**Core length (cm)**	**Number of samples**	**Sedimentation rate (cm yr^{-1})**	**Estimate date coverage**
Ferraz I station	Martel	32	32	0.35 ± 0.03	1918–2006
Refuge II	Mackelar	15	15	0.26 ± 0.03	1952–2006
Barrel point	Ezcurra	15	14	0.33 ± 0.03	1963–2006

Table S4. Grain size, elementary (TOC and TN), isotopic composition, (δ^{13}C and δ^{15}N) and C/N ratio in austral summer of 2020 in Admiralty Bay, King George Island. TOC: Total Organic Carbon; TN: Total Nitrogen.

	Site (code)	**TOC (%)**	**TN (%)**	**δ^{13}C (‰)**	**δ^{15}N (‰)**	**C/N**	**Carbonate (%)**	**Silt + clay (%)**
Martel Inlet	P01	0.165	0.012	-24.58	22.66	16.04	18.73	60.25
	P02	0.247	0.022	-25.73	19.70	13.10	12.70	27.37
	P08	0.512	0.096	-22.34	7.02	6.22	12.48	38.94
	P09	0.950	0.140	-21.33	5.60	7.92	14.31	28.96
	P10	0.887	0.184	-24.08	7.38	5.62	18.29	79.90
	P11	0.986	0.170	-19.20	5.82	6.77	18.49	40.54
	P12	0.808	0.121	-23.88	3.82	7.79	22.46	47.63
	P13	0.331	0.051	-18.43	10.05	7.57	18.63	65.01
Mackelar Inlet	P03	0.333	0.032	-25.89	11.88	12.14	11.06	93.38
	P04	0.180	0.015	-25.45	19.57	14.00	6.68	14.98
	P05	0.488	0.076	-23.10	6.41	7.49	15.52	56.41
	P06	0.493	0.045	-24.29	10.53	12.78	17.66	78.63
Ezcurra Inlet	P14	0.105	0.027	-24.14	-10.42	4.54	8.79	5.39
	P15	0.092	0.025	-23.54	-7.68	4.29	10.15	7.03
	P16	0.121	0.057	-23.45	-4.02	2.48	11.57	10.13
	P17	0.340	0.059	-19.85	8.61	6.72	14.85	41.59
	P18	0.397	0.051	-22.67	9.87	9.08	16.91	97.03
Minimum		0.092	0.012	-25.89	-10.42	2.48	6.68	5.39
Maximum		0.986	0.184	-18.43	22.66	16.04	22.46	97.03
Mean ± SD		0.437 ± 0.292	0.070 ± 0.052	-23.06 ± 2.15	7.46 ± 8.65	8.50 ± 3.70	14.66 ± 4.10	46.66 ± 28.58

Table S5. Elementary (TOC and TN), isotopic composition, ($\delta^{13}C$ and $\delta^{15}N$), carbonate and C/N ratio in the surficial sediments sampled between austral summer of 2013 and 2020 from Admiralty Bay, Antarctica. TOC: Total Organic Carbon; TN: Total Nitrogen.

	Site (code)	**Sampling date**	**TOC (%)**	**TN (%)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**C/N**	**Carbonate (%)**
Martel Inlet **Ferraz Station I (Fer)**	P9	2020	0.950	0.140	-21.33	5.61	7.92	14.31
	Fer-S1	2019	0.415	0.064	-23.57	9.20	7.57	18.49
	Fer-S2	2018	0.441	0.066	-22.94	1.18	7.80	15.28
	Fer-S3	2017	0.553	0.079	-24.05	6.24	8.17	17.52
	Fer-S4	2016	0.454	0.073	-22.72	1.38	7.26	16.37
	Fer-S5	2015	0.509	0.084	-23.81	1.50	7.07	17.94
	Fer-S6	2014	0.380	0.090	-23.99	2.32	4.93	14.95
	Fer-S7	2013	0.526	0.090	-22.28	-0.07	6.82	15.27
	Minimum		0.380	0.064	-24.05	-0.07	4.93	14.31
	Maximum		0.950	0.140	-21.33	9.20	8.17	18.49
	Mean ± SD		0.529 ± 0.168	0.086 ± 0.023	-23.09 ± 0.89	3.42 ± 3.01	7.19 ± 0.95	16.27 ± 1.45

Table S5 (continued).

	Site (code)	**Sampling date**	**TOC (%)**	**TN (%)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**C/N**	**Carbonate (%)**
Mackelar Inlet **Refuge II (Ref)**	P6	2020	0.493	0.045	-24.29	10.53	12.78	17.66
	Ref-S1	2019	0.401	0.061	-22.82	-1.54	7.67	15.26
	Ref-S2	2018	0.341	0.042	-22.43	-4.90	9.47	13.54
	Ref-S3	2017	0.474	0.037	-24.73	-5.03	14.95	14.97
	Ref-S4	2016	0.530	0.032	-23.62	-8.58	19.32	13.94
	Ref-S5	2015	0.456	0.052	-22.37	-2.90	10.23	15.71
	Ref-S6	2014	0.477	0.082	-23.61	-5.16	6.79	15.60
	Ref-S7	2013	0.370	0.030	-22.23	-8.37	14.39	14.15
	Minimum		0.341	0.030	-24.73	-8.58	6.79	13.54
	Maximum		0.530	0.082	-22.23	10.53	19.32	17.66
	Mean ± SD		0.443 ± 0.061	0.048 ± 0.016	-23.26 ± 0.88	-3.24 ± 5.67	11.95 ± 3.94	15.10 ± 1.22

Table S5 (continued).

	Site (code)	Sampling date	TOC (%)	TN (%)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	C/N	Carbonate (%)
Ezcurra Inlet **Barrel point (Bar)**	P18	2020	0.397	0.051	-22.67	9.87	9.08	16.91
	Bar-S1	2017	0.314	0.060	-24.62	-12.41	6.11	14.98
	Bar-S2	2015	0.524	0.041	-24.60	-12.44	14.91	12.35
	Bar-S3	2014	0.429	0.060	-24.20	-4.28	8.34	14.21
	Bar-S4	2013	0.483	0.065	-23.29	-0.59	8.67	17.00
	Minimum		0.314	0.041	-24.62	-12.44	6.11	12.35
	Maximum		0.524	0.065	-22.67	9.87	14.91	17.00
	Mean ± SD		0.429 ± 0.072	0.055 ± 0.008	-23.88 ± 0.77	-3.97 ± 8.32	9.42 ± 2.93	15.09 ± 1.75

Table S6. Elementary and isotopic composition (TOC, TN, $\delta^{13}C$ and $\delta^{15}N$), carbonates and C/N ratio in the Ferraz I (Fer) sediment core, Admiralty Bay, Antarctica. TOC: Total Organic Carbon; TN: Total Nitrogen.

Site (code)	**Estimated date**	**Depth (cm)**	**TOC (%)**	**TN (%)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**C/N**	**Carbonate (%)**
Fer-T1	2007	0.5	0.667	0.101	-25.46	2.32	7.70	17.37
Fer-T2	2004	1.5	0.625	0.093	-25.69	3.95	7.84	18.37
Fer-T3	2001	2.5	0.602	0.117	-25.54	2.14	2.14	18.28
Fer-T4	1998	3.5	0.515	0.084	-25.68	3.23	7.15	18.94
Fer-T5	1995	4.5	0.479	0.067	-25.28	1.42	8.34	19.80
Fer-T6	1992	5.5	0.421	0.060	-25.42	2.52	8.19	19.84
Fer-T7	1989	6.5	0.460	0.068	-25.12	-0.73	7.65	20.23
Fer-T8	1987	7.5	0.400	0.062	-25.61	-1.53	7.53	20.96
Fer-T9	1984	8.5	0.437	0.058	-25.29	1.98	8.79	15.33
Fer-T10	1981	9.5	0.402	0.058	-25.38	2.13	8.09	19.97
Fer-T11	1978	10.5	0.367	0.054	-25.58	1.43	7.93	19.90
Fer-T12	1975	11.5	0.397	0.056	-25.15	5.17	8.27	20.38
Fer-T13	1972	12.5	0.382	0.053	-25.25	3.42	8.41	18.94
Fer-T14	1969	13.5	0.364	0.043	-25.50	6.38	9.88	20.47
Fer-T15	1967	14.5	0.458	0.049	-25.10	8.46	10.90	19.46
Fer-T16	1964	15.5	0.418	0.057	-25.25	9.41	8.56	19.86
Fer-T17	1961	16.5	0.431	0.054	-25.60	6.76	9.31	19.55
Fer-T18	1958	17.5	0.403	0.061	-25.35	4.50	7.71	22.61
Fer-T19	1955	18.5	0.393	0.081	-25.52	3.31	5.66	20.42
Fer-T20	1952	19.5	0.422	0.068	-25.41	2.53	7.24	19.23
Fer-T21	1949	20.5	0.477	0.057	-25.29	5.17	9.76	18.79
Fer-T22	1947	21.5	0.419	0.073	-25.08	1.32	6.70	19.64
Fer-T23	1944	22.5	0.413	0.063	-25.47	3.24	7.65	20.39
Fer-T24	1941	23.5	0.428	0.060	-25.44	7.36	8.32	20.79
Fer-T25	1938	24.5	0.441	0.074	-25.36	0.95	6.95	19.79
Fer-T26	1935	25.5	0.442	0.054	-25.19	10.84	9.55	19.61
Fer-T27	1932	26.5	0.422	0.053	-25.35	10.12	9.29	19.76
Fer-T28	1929	27.5	0.388	0.057	-25.63	6.61	7.94	17.62
Fer-T29	1927	28.5	0.402	0.057	-25.50	11.63	8.23	19.16
Fer-T30	1924	29.5	0.394	0.047	-24.91	8.55	9.78	19.74
Fer-T31	1921	30.5	0.403	0.051	-25.43	9.18	9.22	20.92

Fer-T32	1918	31.5	0.406	0.057	-25.47	7.24	8.31	20.36
Minimum			0.36	0.04	-25.69	-1.53	5.66	15.33
Maximum			0.67	0.12	-24.91	11.63	10.90	22.61
Mean ± SD			0.44 ± 0.07	0.06 ± 0.02	-25.38 ± 0.19	4.72 ± 3.40	8.21 ± 1.12	19.58 ± 1.26

Table S7. Elementary and isotopic composition (TOC, TN, $\delta^{13}C$ and $\delta^{15}N$), carbonates and C/N ratio in the Refuge II (Ref) sediment core, Admiralty Bay, Antarctica. TOC: Total Organic Carbon; NT: Total Nitrogen.

Site (code)	**Estimated date**	**Depth (cm)**	**TOC (%)**	**TN (%)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**C/N**	**Carbonate (%)**
Ref-T1	2006	0.5	0.418	0.100	-23.51	-6.07	4.88	17.44
Ref-T2	2002	1.5	0.523	0.093	-23.66	-4.76	6.56	16.26
Ref-T3	1998	2.5	0.466	0.052	-25.01	-1.06	10.46	16.80
Ref-T4	1995	3.5	0.360	0.091	-23.56	-4.47	4.62	16.75
Ref-T5	1991	4.5	0.518	0.105	-23.28	-3.94	5.76	18.48
Ref-T6	1987	5.5	0.532	0.103	-23.38	-0.95	6.03	18.15
Ref-T7	1983	6.5	0.540	0.082	-24.20	-1.58	7.68	17.78
Ref-T8	1979	7.5	0.494	0.056	-24.05	0.34	10.29	16.69
Ref-T9	1975	8.5	0.381	0.060	-24.29	-4.03	7.41	14.00
Ref-T10	1971	9.5	0.384	0.061	-24.30	-9.86	7.34	16.61
Ref-T11	1968	10.5	0.343	0.058	-24.93	-3.38	6.90	16.80
Ref-T12	1964	11.5	0.335	0.114	-22.68	-1.52	3.43	21.83
Ref-T13	1960	12.5	0.605	0.053	-24.63	-9.31	13.32	18.61
Ref-T14	1956	13.5	0.290	0.039	-24.36	0.91	8.68	18.24
Ref-T15	1952	14.5	0.290	0.042	-24.36	2.02	8.06	14.27
	Minimum		0.29	0.04	-25.02	-9.86	3.43	14.00
	Maximum		0.61	0.11	-22.68	2.02	13.32	21.83
	Mean ± SD		0.43 ± 0.10	0.07 ± 0.02	-24.01 ± 0.63	-3.18 ± 3.33	7.43 ± 2.45	17.25 ± 1.79

Table S8. Elementary and isotopic composition (TOC, TN, $\delta^{13}C$ and $\delta^{15}N$), carbonates and C/N ratio in the Barrel point (Bar) sediment core, Admiralty Bay, Antarctica. TOC: Total Organic Carbon; NT: Total Nitrogen.

Site (code)	**Estimated date**	**Depth (cm)**	**TOC (%)**	**TN (%)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**C/N**	**Carbonate (%)**
Bar-T1	2006	0.5	0.232	0.018	-24.13	0.06	15.04	15.56
Bar-T2	2003	1.5	0.270	0.044	-22.86	-3.69	7.16	15.82
Bar-T3	1999	3.0	0.242	0.026	-24.05	-9.03	10.86	15.77
Bar-T4	1994	4.5	0.229	0.025	-24.39	-5.80	10.69	15.90
Bar-T5	1991	5.5	0.235	0.074	-24.40	-6.80	3.70	14.62
Bar-T6	1988	6.5	0.241	0.018	-23.95	1.12	15.62	14.42
Bar-T7	1985	7.5	0.241	0.023	-23.29	-9.40	12.22	14.58
Bar-T8	1982	8.5	0.232	0.016	-24.05	2.27	16.92	14.64
Bar-T9	1979	9.5	0.243	0.019	-23.67	-4.97	14.92	15.01
Bar-T10	1976	10.5	0.218	0.019	-24.48	1.18	13.39	14.86
Bar-T11	1973	11.5	0.210	0.017	-24.57	0.04	14.41	14.97
Bar-T12	1970	12.5	0.214	0.020	-24.91	-10.66	12.48	14.77
Bar-T13	1967	13.5	0.207	0.016	-24.68	0.53	15.09	15.03
Bar-T14	1963	15.0	0.207	0.044	-24.94	-5.95	5.49	15.10
Minimum			0.21	0.02	-24.94	-10.66	3.70	14.42
Maximum			0.27	0.07	-22.86	2.27	16.92	15.90
Mean ± SD			0.23 ± 0.02	0.03 ± 0.02	-24.17 ± 0.57	-3.65 ± 4.29	12.00 ± 3.88	15.08 ± 0.48