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DETERMINAÇÃO DE CARBONO NEGRO SEDIMENTAR A NÍVEL MOLECULAR EM ZONAS COSTEIRAS TROPICAIS

TASSIANA SOARES GONÇALVES SERAFIM

Orientador: Prof. Carlos Eduardo de Rezende (LCA/CBB/UENF)

CAMPOS DOS GOYTACAZES – RJ
Setembro – 2021

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RESUMO

A modificação do uso do solo de floresta para plantações e áreas de pastagem além de modificar a paisagem, altera a qualidade da matéria orgânica (MO) do solo. Atualmente, cerca de 15 e 74 % dos biomas da Amazônia e Mata Atlântica, respectivamente, apresentam uma forte modificação da paisagem como consequência às alterações antrópicas. Uma estratégia muito utilizada para remoção de biomassa florestal e manejo das áreas de plantações e de pastagem é a utilização do fogo. A combustão incompleta da biomassa produz MO termicamente modificada que, globalmente, representa cerca de 14 % da MO encontrada no solo, e é comumente denominada de carbono negro (CN). A entrada de CN associado às partículas nos sistemas aquáticos ocorre a partir do transporte lateral e, sua deposição no compartimento sedimentar ocorre ao longo do gradiente continente-oceano. O trabalho investigou a dinâmica e a concentração de CN em sedimentos de zonas costeiras em bacias de drenagem principalmente cobertas por florestas (plantas C_3): zonas costeiras dos rios Sinnamary (FG_{CZ}) e Amazonas (AM_{CZ}), e na zona costeira do rio Paraíba do Sul (PSR_{CZ}), coberta principalmente por gramíneas (plantas C_4) devido às modificações antrópicas. Para identificar as fontes que contribuem para a MO sedimentar, a composição isotópica de carbono ($\delta^{13}C$) foi determinada a partir do analisador elementar Flash 2000 acoplado a um espectrômetro de massa Delta V e o CN foi determinado a partir da oxidação da MO e formação de seus marcadores moleculares nos equipamentos: GC-MS e HPLC. O $\delta^{13}C$ da PSR_{CZ} apresentou valores enriquecidos em ^{13}C (-22,6 ± 1,3 ‰, $p < 0,01$) quando comparados as AM_{CZ} e FG_{CZ} (-25,0 ± 3,1 e -26,1 ± 1,0 ‰, respectivamente), indicando que a alteração do uso do solo na bacia pode estar modificando a MO transportada. O teor de CN, normalizado ao teor de carbono orgânico (CO) do sedimento, foi menor na AM_{CZ} (0,32 ± 0,24 mg g^{-1} CO), provavelmente devido à alta descarga do rio e a deposição de CN em locais intermediários. FG_{CZ} e PSR_{CZ} apresentaram concentrações semelhantes de CN (0,73 ± 0,67 e 0,95 ± 0,74 mg g-1 OC, respectivamente, $p = 0,759$), mas com fontes diferindo de acordo com a atual cobertura vegetal das bacias. Na FG_{CZ}, o CN foi rapidamente degradado ao longo do gradiente de condutividade elétrica (EC), o que sugere que o CN pode ser composto principalmente de carbono lábil susceptível à degradação rápida. Na PSR_{CZ}, o conteúdo de CN aumenta no gradiente EC e o grau de condensação não varia, indicando dominância de carbono estável e possível deposição atmosférica de fuligem. Na AM_{CZ}, o conteúdo de CN não varia ao longo do gradiente EC, mas o grau de condensação mostra que a deposição de CN pode ter dois mecanismos: CN envelhecido do transporte fluvial e remoção do componente hidrofóbico do CN dissolvido. Amostras com altos valores de EC exibiram teor de CN, o que evidencia o transporte de material terrestre refratário para as zonas costeiras.

ABSTRACT

The land-use change from forest to cultivated plantations and pasture areas, besides modifying the landscape, alters the quality of organic matter (OM) in the soil. Currently, about 15 and 74 % of the Amazon and Atlantic Forest biomes, respectively, present a strong modification of the landscape as a consequence of anthropogenic alterations. A widely used strategy for removing forest biomass and managing plantation and pasture areas is the use of fire. The incomplete combustion of biomass produces thermally modified OM which, globally, represents about 14 % of the OM present in the soil, and is commonly known as black carbon (BC). The input of particle-associated BC into aquatic systems occurs from lateral transport and, its deposition into the sediment compartment occurs along the continent-ocean gradient. The study investigated the dynamics and concentration of BC in sediments of coastal zones in drainage basins mainly covered by forests (C_3 plants): coastal zones of the Sinnamary (FG_{CZ}) and Amazon rivers (AM_{CZ}), and in the coastal zone of the Paraíba do Sul river (PSR_{CZ}), covered mainly by grasses (C_4 plants) due to anthropogenic modifications. To identify the sources contributing to the sediment OM, the carbon isotopic composition ($\delta^{13}C$) was determined from the Flash 2000 elemental analyzer coupled to a Delta V mass spectrometer, and BC was determined from the oxidation of OM and formation of its molecular markers in the equipment: GC-MS and HPLC. The $\delta^{13}C$ of the PSR_{CZ} showed ^{13}C-enriched values (-22.6 ± 1.3 ‰, $p < 0.01$) when compared to the AM_{CZ} and FG_{CZ} (-25.0 ± 3.1 and -26.1 ± 1.0 ‰, respectively), indicating that land-use change in the basin may be modifying the transported OM. The BC content, normalized to the organic carbon (OC) content of the sediment, was lower in the AM_{CZ} (0.32 ± 0.24 mg g-1 OC), probably due to the high river discharge and the deposition of BC at intermediate sites. FG_{CZ} and PSR_{CZ} showed similar BC content (0.73 ± 0.67 and 0.95 ± 0.74 mg g^{-1} OC, respectively, $p = 0.759$), but with sources differing according to the current vegetation cover of the basins. In the FG_{CZ}, BC has rapidly degraded along with the electrical conductivity (EC) gradient, suggesting that BC may be composed mainly of labile carbon susceptible to rapid degradation. In the PSR_{CZ}, BC content increases along the EC gradient, and the degree of condensation does not vary, indicating the dominance of stable carbon and possible atmospheric soot deposition. In the AM_{CZ}, BC content does not vary along the EC gradient, but the degree of condensation shows that BC deposition may have two mechanisms: aged BC from river transport and removal of the hydrophobic component of dissolved BC. Samples with high EC values exhibited BC content, which evidences the transport of refractory terrestrial material to the coastal zones.

1. INTRODUÇÃO GERAL

Incêndios florestais e queima de vegetação atingem anualmente cerca de 4 % da biomassa global (Randerson et al., 2012). A queima incompleta de biomassa vegetal produz uma forma enriquecida em carbono que apresenta caráter refratário e pode ser resistente à degradação: o carbono negro (CN; Goldberg, 1985). Estas características somadas à sua presença em todos os compartimentos ambientais o torna um importante componente do ciclo do carbono (Bird e Ascough, 2012; Santín et al., 2016; Coppola et al., 2018). O CN é comumente apresentado como um modelo de combustão contínua onde os produtos variam desde matéria orgânica levemente alterada a compostos aromáticos policíclicos altamente condensados (Figura 1; Masiello, 2004; Coppola e Druffel, 2016). Todos os compostos deste modelo apresentam elevado conteúdo de carbono e são quimicamente heterogêneos (Masiello, 2004). Esta heterogeneidade e a alta complexidade resultam na elevada resistência à oxidação química e térmica e em diferentes taxas de reatividade da molécula (Schmidt e Noack, 2000; Jones et al., 2017) diferindo da matéria orgânica não termicamente alterada (Glaser et al., 1998). A característica inerte é observada principalmente nos compostos mais condensados do modelo, o que resulta na baixa formação de CO_2 fazendo com que o CN se torne um sumidouro de carbono (Forbes et al., 2006).

Características	**Matéria orgânica levemente carbonizada**	**Matéria orgânica carbonizada**	**Carvão vegetal**	**Cinza**	**Grafite**
Tamanho	mm ou maior		mm a µm	µm	
Reservatório inicial	solos		solos e atmosfera		
Alcance	m	m a km		km	
Reatividade: (O:C)a	0,8	0,6	0,4	0,2	0

Figura 1. Modelo do "contínuo" de combustão de CN. Adaptado de Hedges et al. (2000) e Masiello (2004).

O CN produzido em bacias de drenagem compõem, a nível mundial, cerca de 14 % da matéria orgânica do solo (Reisser et al., 2016) e, de acordo com Kuhlbusch e Crutzen (1995), aproximadamente 80 % do material pirogênico produzido fica inicialmente no solo próximo ao local de produção. O tempo de residência no solo pode chegar a centenas de anos e a variação das taxas de decomposição de CN encontradas é resultado dos diferentes mecanismos que podem modificar fisicamente e quimicamente a molécula de CN (Singh et al., 2012; Wang et al., 2013), bem como sua estabilização em escala local (Wang et al., 2016). A remoção de CN do solo e a entrada no sistema aquático, se dão através de sua solubilização por ação de organismos microbianos (Dittmar et al., 2012) e pelo transporte lateral de partículas (Major et al., 2010) que ocorre principalmente após erosão e consequente lixiviação do solo após eventos de precipitação. Além disso, os compostos altamente condensados podem também ser transportados via atmosfera na forma de fuligem e serem depositados longe de seu local de produção (Figura 1; Masiello, 2004). Assim, a presença de CN em rios, zonas de transição e no oceano se devem também à deposição atmosférica e não somente ao transporte fluvial (Hockaday et al., 2007; Coppola et al., 2014), embora este seja o processo majoritário na mobilização de CN para esses ecossistemas aquáticos (Forbes et al., 2006; Coppola et al., 2018).

Sistemas fluviais através de suas zonas estuarinas conectam os ciclos de carbono terrestre e marinho (Coppola et al., 2018) transportando cerca de 2,7 Pg de carbono terrestre por ano para os oceanos (Aufdenkampe et al., 2011). Parte deste carbono orgânico é conservado ao longo do gradiente continente – oceano e, o CN compõe cerca de 10 e 16 % do carbono orgânico dissolvido e particulado encontrados em rios, respectivamente (Jaffé et al., 2013; Coppola et al., 2018; Jones et al., 2019). A fração particulada está constantemente sujeita a deposição acarretando no acúmulo de CN no compartimento sedimentar ao longo do gradiente (Schmidt e Noah, 2000). No sedimento, o CN pode constituir até 50 % do carbono orgânico (Middelburg et al., 1999) adsorvido principalmente nas partículas finas, como silte e argila. Entretanto, no compartimento sedimentar marinho sua mobilização representa de 3 a 10 % do fluxo global de CN (Santín et al., 2016). Em consequência ao forte gradiente físico-químico das zonas estuarinas, tem-se a redução considerável do transporte de partículas para o oceano. Em um estudo realizado por Regnier et al. (2013), foi estimado o fluxo de transporte lateral de

partículas ao longo do gradiente continente – oceano e, os autores relataram que globalmente, 50 % do carbono orgânico particulado não alcança o oceano devido à sua deposição em zonas de transição facilitada pelo forte gradiente físico – químico.

Com a finalidade de determinar o CN, diversos métodos analíticos são encontrados na literatura, abordando diferentes espectros do modelo de combustão contínua (Masiello, 2004; Hammes et al., 2007). O método de determinação de CN a partir dos ácidos benzeno-policarboxílicos (BPCA) atua em quase todo o modelo e determina especificamente as porções aromáticas condensadas (Dittmar et al., 2012). Sánchez-García et al. (2013) avaliaram a concentração de CN em sedimentos do golfo de Cádiz (Espanha) comparando dois métodos na determinação de CN: a partir dos BPCA e a partir de termo oxidação (GBC), este identifica a porção mais aromática do “contínuo”. Os autores encontraram diferentes concentrações de CN devido à diferença da amplitude da determinação dos compostos. No método utilizando os marcadores moleculares, o CN compôs 11 ± 10 % do carbono orgânico, enquanto o método GBC o material pirogênico compunha 5 ± 3 %, assim, a comparação entre diferentes métodos pode levar a subestimação do conteúdo de CN.

Os marcadores moleculares de CN são obtidos a partir da oxidação da molécula com ácido nítrico em alta temperatura e pressão com posterior isolamento e quantificação dos BPCA para estimar o conteúdo de CN e, são considerados marcadores específicos para determinação à nível molecular de CN (Dittmar, 2008). A oxidação converte o CN em anéis de benzeno que apresentam números de grupos de ácidos carboxílicos que podem variar entre 3 a 6 grupos (Figura 2; Brodowski et al., 2005).

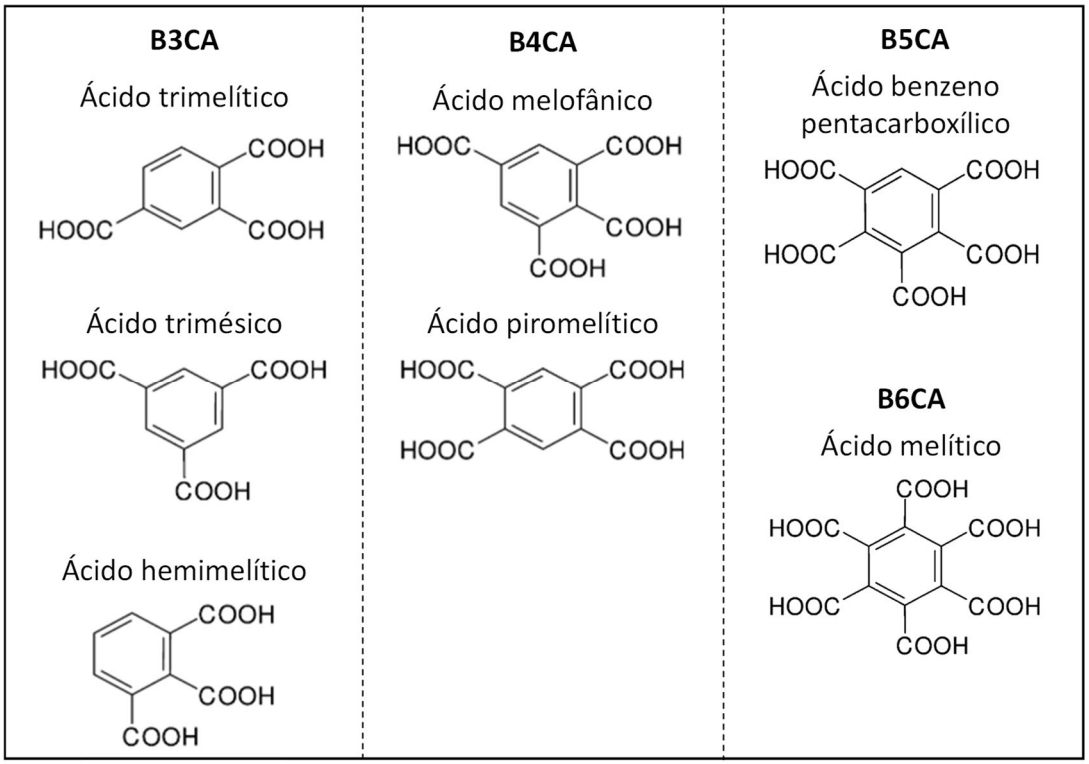

Figura 2. Ácidos benzeno policarboxílicos formados a partir da oxidação da molécula de CN. Modificado de Brodowski et al. (2005).

Ao avaliar a existência de um padrão sistemático na produção de BPCA, Schneider et al. (2010) avaliaram sua distribuição em intervalos de temperatura de combustão de biomassa variando entre 200 e 1000 °C. Os autores observaram um aumento da produção dos grupos com 5 e 6 ácidos carboxílicos, ácidos benzeno pentacarboxílico (B5CA) e melítico (B6CA), respectivamente, com o aumento da temperatura, além do aumento do conteúdo de CN (Figura 3). Embora a temperatura de combustão pareça reger as propriedades físicas e químicas da matéria orgânica termicamente modificada (Brown et al., 2006), outros parâmetros podem também influenciar na produção, tais como: tipo de fonte de biomassa vegetal, oxigênio, duração da combustão e/ou condições do vento (Schneider et al., 2010; Wolf et al., 2013; Budai et al., 2017). A faixa de temperaturas típicas para queima de biomassa próximo à superfície do solo varia de 275 a 500 °C e pode alcançar 800 °C para incêndios de vegetação arbórea (Alexis et al., 2007), nestas circunstâncias, o B5CA e o B6CA compõem entre 70 e 95 % da molécula de CN gerado a partir da queima incompleta de biomassa vegetal (Schneider et al., 2010).

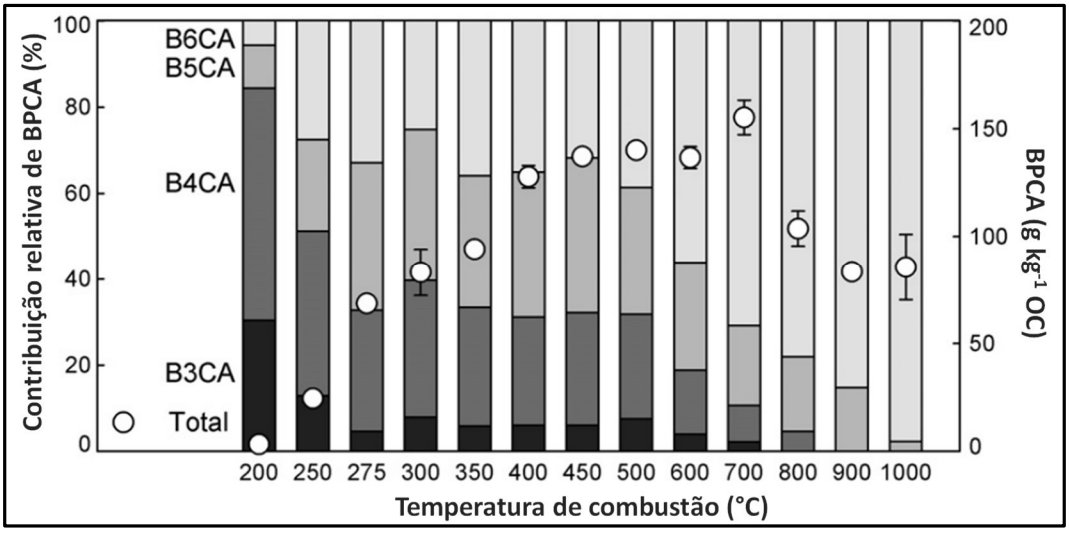

Figura 3. Conteúdo de CN (círculos brancos, escala direita) produzidos a temperaturas crescentes de carbonização e a contribuição relativa do BPCA individual para o conteúdo total do carbono negro (escala esquerda). Modificado de Schneider et al. (2010).

A contribuição individual dos marcadores moleculares de CN é usada para avaliar o tamanho dos compostos aromáticos de uma amostra ou o seu grau de condensação. Enquanto que os marcadores B3CA, B4CA e B5CA podem ser produzidos a partir de anéis na margem externa da molécula, o B6CA só é originado a partir de seu núcleo (Schneider et al., 2010). Apesar deste método avaliar quantitativamente e qualitativamente os marcadores moleculares, o método apresenta algumas limitações: em amostras com peso de CO superior a 5 mg, os BPCA são produzidos a partir de MO não termicamente modificada (Kappenberg et al., 2016). Portanto, ao avaliar a concentração e a dinâmica do CN e comparar com outros trabalhos essas limitações (bem como uso de diferentes técnicas) devem ser consideradas a fim de não superestimar ou subestimar os processos que ocorrem desde a produção ao destino final do CN.

2. OBJETIVO

O trabalho teve como objetivo geral analisar o conteúdo de CN e sua dinâmica em zonas costeiras de rios com coberturas vegetais distintas a partir da determinação do CN a nível molecular.

2.1. Objetivos específicos

Avaliar através da ferramenta dos isótopos estáveis do carbono e nitrogênio as fontes que contribuem para a matéria orgânica do compartimento sedimentar das zonas costeiras estudadas e, adicionalmente, avaliar se a ferramenta isotópica pode ajudar a elucidar a questão acerca da produção de CN nas bacias de drenagem.

3. RESULTADOS

Os resultados produzidos durante o período de mestrado serão apresentados na forma de artigo científico a seguir:

3.1. Artigo científico: **Carbon isotopic composition and black carbon dynamics in surface sediments under Amazon and Atlantic rainforest influence**

Carbon isotopic composition and black carbon dynamics in surface sediments under Amazon and Atlantic rainforest influence

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Abstract: Our research investigated the dynamics and concentration of black carbon (BC) and the carbon isotopic composition ($\delta^{13}C$) of organic matter (OM) in coastal sediments in drainage basins mainly covered by forested (Amazon Rainforest – C_3 plants): coastal zones of the Sinnamary and Amazon River; as well as the coastal zone of the Paraíba do Sul River (PSR), which is mainly covered by grasses (Atlantic Rainforest – C_4 plants). The results showed the $\delta^{13}C$ was more ^{13}C-enriched in PSR coastal sediments (-22.6 ± 1.3 ‰, $p < 0.01$) when compared to the Amazon and Sinnamary (-25.0 ± 3.1 ‰ and -26.1 ± 1.0 ‰, respectively), indicating that the land-use changes in the basin have probably modified the quality of OM in the sediment of PSR coastal zone. BC content, normalized by the organic carbon content, was lower in the Amazon sediments (0.32 ± 0.24 mg g^{-1} OC). The Sinnamary and PSR coastal zones had similar concentrations (0.73 ± 0.67 and 0.95 ± 0.74 mg g^{-1} OC, respectively), but the sources for BC content differed according to the vegetation cover of the basins. Along with the electrical conductivity (EC) gradient, BC content decreased in the Sinnamary coastal zone, suggesting that BC might be susceptible to faster degradation. In the PSR coastal zone, the BC content increased, while the degree of condensation did not change, indicating stable carbon dominance and possible atmospheric deposition of soot. In the Amazon coastal zone, BC content did not change along the EC gradient, but the degree of condensation showed that BC in sediments may have two mechanisms: aged BC from river transport and removal of the hydrophobic component of dissolved BC. Different sources and transformations act on the concentrations and dynamics of BC in coastal zones.

Keywords: Black carbon, Amazon Rainforest, Atlantic Rainforest, Carbon isotopic composition, Sediments.

INTRODUCTION

In Brazil, the conversion of primary forest areas for cropland and agriculture has devastated the Atlantic rainforest and continues to destroy important biomes such as the world's largest forest, the Amazon rainforest (Ferrante and Fearnside, 2019), modifying qualitatively the organic matter (OM) present in the soil (Bernardes et al., 2004). The conversion of native forest vegetation has altered the Atlantic rainforest landscape, of which about 28 % of its original vegetation cover remains distributed in fragments (Rezende et al., 2018; Solórzano et al., 2021). Such anthropogenic areas currently comprise approximately 15 % of the Amazon biome (Stahl et al., 2016) and are increasing due to the invasion of forest areas. One strategy for forest biomass removal and the management of anthropic areas is the use of fire as a tool (Edwards, 1984), which is the main vector for biomass removal in the Amazon rainforest today through forest fires caused by drought events (Aragão et al., 2018) and anthropogenic activities, such as the management of cattle pasture and agricultural areas. It is estimated that globally anthropogenic forest fires and anthropogenic burning emit about 2.2 Pg of carbon per year into the atmosphere in the form of greenhouse gases (Werf et al., 2017). In addition, fires produce another carbon-enriched form that exhibits greater resistance to degradation compared to non-altered thermally OM, black carbon (Forbes et al., 2006; Bird and Ascough, 2012).

Black carbon (BC) is the commonly used term to describe the thermally altered OM produced after incomplete combustion of plant biomass or fossil fuels (Goldberg, 1985). Hedges et al. (2000) described the broad spectrum of BC compounds as a combustion "continuum" model, which was later described as a degradation continuum that varies from slightly altered biomass susceptible to rapid degradation to highly condensed aromatic compounds that can persist in the environment (Masiello, 2004; Bird et al., 2015). The global production of BC derived from plant biomass releases between 50 and 300 Tg of BC per year (Forbes et al., 2006; Bird et al., 2015) and it is estimated that 80 % of BC initially remains at its production site after combustion (Kuhlbusch and Crutzen, 1995). According to Reisser et al. (2016), globally, BC constitutes about 14 % of soil OM with an average residence time in the compartment of 88 years, in a period that can range from a few years to millennia, depending on the combination of physical, chemical, and

microbial processes taking place in the OM degradation (Singh et al., 2012). The removal of BC from the soil and its entry into the aquatic system occurs mainly through the transport of the dissolved phase after solubilization of historical BC (Dittmar, 2008; Dittmar et al., 2012) and lateral particle transport resulting mainly from soil erosion (Major et al., 2010). In addition, to a smaller extent, the input of BC into aquatic systems can occur via atmospheric transport, and its deposition can occur along the entire continent – ocean gradient (Jurado et al., 2008; Coppola et al., 2018).

Increased erosion due to land use conversion increases the transport of particles to the aquatic system, resulting in the global accumulation of 75 Tg per year of sediments from areas below 2000 m altitude (Wilkinson and McElroy, 2007; Bird et al., 2015). These eroded particles are deposited along the continent – ocean gradient, mostly in continental areas and in transition zones. About 20 % of this material reaches its final destination: the marine sediment compartment (Rumpel et al., 2009; Bird et al., 2015). By estimating the flux of BC in the particulate fraction of the water column and sediments of large (e.g., the Amazon, Congo) and small rivers (e.g., the Eel, Santa Clara, Danube), Coppola et al. (2018) observed that BC comprises about 15.8 ± 0.9 % of the organic carbon (OC) present in the suspended particulate matter (SPM) and sediments. Furthermore, the authors attributed the export dynamics of BC in the rivers as resulting from soil erosion.

The global flux of OC associated with SPM to the ocean ranges from 19 to 80 Tg per year (Bird et al., 2015). This flux and the quality of the pyrogenic material associated with the SPM to coastal zones can be influenced by the characteristics of rivers and their drainage basins (Burdige, 2007). In small rivers usually associated with mountains, narrow continental shelves, or active continental margins, the transport of eroded material to the coastal zone occurs more rapidly with relatively low remineralization rates of OM along the continent – ocean gradient (Blair et al., 2003; Burdige, 2007). In contrast, in large rivers and deltas, SPM is subject to cycles of deposition and resuspension, and as a result of these processes, there is increased remineralization of OM due to long residence times (Aller, 1998). Additionally, the OM (or BC) associated with the SPM transported can be replaced downstream by OM produced at lower elevations, and/or dilution can also affect its flux (Aller et al., 1996; Burdige, 2007). The transport of particles to the ocean is considerably reduced due to the strong physicochemical gradient in the estuarine

zones, which favorites processes such as flocculation. Regnier et al. (2013), by analyzing the lateral transport flux of particulate matter to coastal zones, observed that, globally, 50 % of particulate OC does not reach the ocean due to its deposition in transition zones.

Thus, the present study sought to evaluate the dynamics and concentration of BC in the sediment compartment of coastal zones of basins with primary forest vegetation cover (terrestrial plants with photosynthetic cycle C_3): coastal zones of the Sinnamary and Amazon rivers; and, as a result of land-use change, a basin mostly covered by grasses (terrestrial plants photosynthetic cycle C_4): coastal zone of the Paraíba do Sul river (PSR), to evaluate if the modification of primary forest areas to pasture and cultivation areas changed the OM deposited in the sediment compartment of the coastal zone. To answer this question, we analyzed the content of BC using its molecular markers, the benzene-polycarboxylic acids (BPCA), as well as the determination of the elemental and isotopic compositions of bulk organic carbon (OC and $\delta^{13}C$, respectively) and nitrogen (N and $\delta^{15}N$, respectively) of the OM. We hypothesized that I: the PSR sample set presents $\delta^{13}C$ values ^{13}C-enriched due to the modification of the vegetation cover of the basin; II: that the BC content in the coastal zone of the Amazon River is lower as a result of the processes of dilution and replacement of OM from the floodplain; and III: the modification of land use in PSR coastal zone is directly related to the BC content.

MATERIALS AND METHODS

Study Area

The Amazon and French Guiana Coastal Zones

The Amazon rainforest extends over several countries, including French Guiana, and has an area representing about 45 % of the world's remaining tropical forests (Laurance et al., 2001), or approximately 4 % of the Earth's surface (about 6,100,000 km^2) (Malhi et al., 2008; Gallo and Vinzon, 2015). In addition to playing an important role in carbon storage in the Amazon's vegetation biomass, the transport of terrestrial carbon to the ocean takes place via the Amazon River (Cai et al.,1988; Malhi et al., 2006; Malhi et al., 2008).

The Amazon River has a seasonal cycle with a maximum discharge reaching an average of 209,000 m^3 s^{-1} during the period from May to July (Latrubesse, 2008). The discharge of materials to the coastal zone comprises approximately 20 % of the global input of terrestrial material to the ocean (Richey et al., 1986; Ward et al., 2015). As a consequence of the basin climate, strong erosion and rapid particle deposition processes can lead to rapid changes in sedimentation rates in the Amazon River plume area (Kuehl et al., 1986). The plume moves in a northwestern direction, and some authors have suggested that a large part of the OM in the sedimentary compartment of the Brazilian shelf and adjacent northwestern areas originates from the Amazon basin (Wells and Coleman, 1981; Nittrouer et al., 1986). Approximately 20 % of the SPM reaching the coastal zone is carried towards French Guiana as a result of the interaction between the Brazilian North Current, the east trade winds, and semi-diurnal sea currents (Geyer et al., 1996; Aller et al., 2004).

Vegetation cover in French Guiana is 97 % tropical forest (Chave et al., 2001) with extensive mangrove forests that occur more than 80 % of the littoral (Fromard et al., 2004). The Sinnamary River, considered a small river, has an average discharge of 237 m^3 s^{-1} with its drainage basin extending over 6,565 km^2 (Richard et al., 2000; Luglia et al., 2019). The Sinnamary River estuary is under a macro tidal regime, with a tidal range around 3 m near its mouth (Ray et al., 2018), which increases the input of leached material from the estuary's extensive mangrove forest dominated by *Avicennia germinans* (Marchand et al., 2003, Marchand, 2017).

The Paraíba do Sul Coastal Zone

The Paraíba do Sul River (PSR) basin, with an area of 57,000 km^2, extends over the states of São Paulo, Rio de Janeiro, and Minas Gerais in the southeast region of Brazil (Ovalle et al., 2013). The PSR occupies an area that was previously and completely covered by the Atlantic rainforest and currently approximately 74 % of the basin is covered by pasture and sugarcane areas (Figueiredo et al., 2011; Marques et al., 2017). As a result of this change, the basin has suffered from an intense erosion process leading to an increase in the contribution of particles to the aquatic system. The PSR estuary and the second largest mangrove forest in the state of Rio de Janeiro are located in São João da Barra, in the Norte Fluminense

region (Bernini and Rezende, 2004). During the dry period, between June and September, the PSR exhibits discharge rates varying between 200 and 500 $m^3 s^{-1}$, while reaching a maximum of 2,600 $m^3 s^{-1}$ during the rainy period (Silva et al., 2001). The PSR is characterized as a small to medium-sized river.

Sampling

Surface sediment samples (0 - 2 cm) were collected following a gradient of electrical conductivity totaling 33 samples distributed in 6, 14, and 13 samples for the coastal zones of the Sinnamary estuary (5°21' - 5°30'N and 52°56' - 53°3'W), the Amazon plume (2°S - 4°N and 46° - 51°W), and the PSR coastal zone (21°28' - 21°40'S and 40°48' - 41°6'W), respectively (Figure 1; Supplementary Table 1). The sample sets were collected during the wet season: on January (2019), April (2018), and February (2014) for Sinnamary estuary, Amazon plume, and PSR coastal zone, respectively.

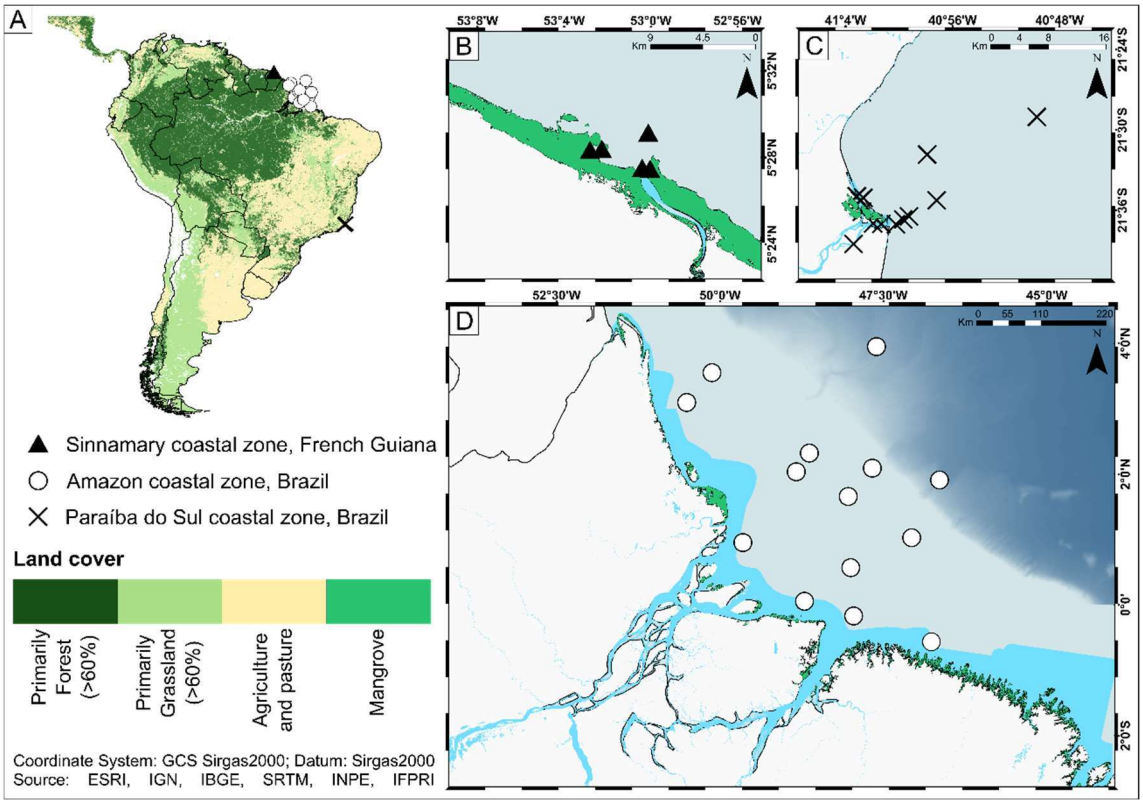

Figure 1. Map representation of the coastal areas of the Sinnamary estuary in French Guiana (B), the Amazonas plume in northern Brazil (D), and the PSR estuary in southeastern Brazil (C).

Elemental and isotopic composition of organic matter

The samples were freeze-dried at the laboratory and homogenized, and 10 mg of sediments were weighed into tin and silver capsules. To obtain OC content and $\delta^{13}C$ composition, the samples were acidified for decarbonation using 2M HCl in silver capsules. The samples were weighed into tin capsules to obtain N and $\delta^{15}N$ values. Elemental and isotopic values were obtained with the Flash 2000 elemental analyzer coupled to a Delta V mass spectrometer, with the detection limit for OC content and $\delta^{13}C$ of 0.05 % and N content and $\delta^{15}N$ values of 0.03 %.

Black Carbon Determination

The method used to determine black carbon was modified from Glaser et al. (1998) and Brodowski et al. (2005). The samples were pre-digested with 10 mL trifluoroacetic acid for 4 h in a high-pressure system at 100 ± 5 °C. The samples were filtered and the filters placed in an oven for 2 h under 40 °C temperature. After drying, for oxidation of the thermally modified OM and consequently obtaining the BPCA, 2 mL of nitric acid were added and the samples were digested at 165 ± 5 °C for 8 h. In 2.5 mL aliquots, 50 µL of the internal standards were added: phytalic and citric acids (1 mg mL^{-1}), for correcting from losses during the cleaning procedure. For purification, the samples were placed in columns with cation exchange resins after conditioning (Dowex 50 WX 8, 200-400 mesh, Fluka, Steiheim, Germany). The eluted volume was separated into 4 vials and freeze-dried to be resuspended with methanol and dried with N_2. To finish “cleaning” the samples, 4 mL of pyridine were added, then the samples were centrifuged and dried once more using N_2. The internal standard biphenyl-2,2’-dicarboxylic acid was added before derivatization of the samples and the BPCA was quantified from its area. The samples were analyzed with gas chromatography (GC/MS) and liquid chromatography (HPLC). For GC/MS analysis, the samples were derivatized with 250 µL of pyridine and 250 µL of BDTFA + TMS with heating for 2 h at 80 °C for subsequent injection into the gas chromatography apparatus with different detectors (GC/FID, GC/MS). For HPLC analysis, after dried with N_2, the samples were resuspended with an aqueous phase

consisting of a tetrabutylammonium bromide solution (4 mM, ACS quality) in phosphate buffer (Na_2HPO_4 and NaH_2PO_4 each 5 mM in ultrapure water, pH 7.2). To allow comparisons of the data obtained from the different equipment, the correction factor of 1.5 suggested by Schneider et al. (2011) was used. To attribute accuracy and precision to the analysis, the standard reference sediment NIST 1941b was used in the determination of the BPCA. The mean BC content normalized by the OC content detected by the GC/MS was 2.08 ± 0.17 mg g^{-1} OC and for HPLC 2.97 ± 0.26 mg g^{-1} OC. The BC content was estimated by the sum of pentacarboxylic (B5CA) and mellitic (B6CA) acids after oxidation with nitric acid. The other groups B3CA and B4CA were not used due to the results observed by Kappenberg et al. (2016), where those two groups were produced after oxidation of non-pyrogenic OM even with low sample weight (< 5 mg OC).

Sources of organic matter in coastal sediments

Bayesian mixing models can provide a synthesis of source and mixture data into a model structure that incorporates the variability of the data (e.g. isotopic fractionation factor) (Parnell et al., 2010) while linear mixing models consider that diagenetic changes do not change significantly the $\delta^{13}C$ and $\delta^{15}N$ values of the OM. Hence, the Bayesian MixSIAR mixing model was used to estimate the contributions of the sources in the sample sets (Stock and Semmens, 2016). The MixSIAR uses Bayesian isotopic mixing and fitting models with Markov chain Monte Carlo (MCMC) simulations of plausible values that are consistent with the dataset (n = 1,000,000, 100,000, and 1,000,000 for Sinnamary, Amazonas, and PSR coastal zones, respectively). The isotopic fractionation factors used were calculated for each area and each possible source (Supplementary Table 2).

Since it is not possible to access the estimative for each sample through the Bayesian models, to evaluate the contribution of the common terrestrial source (terrestrial C_3 plants) for the samples, the two-end-members (Equation 1) (Schultz and Calder, 1976) and three-end-members model (Equation 2) (Fry, 2013) were used:

$$\text{Eq. 1: } C_3 \text{ plants} = \left(\frac{\delta^{13}C_{Marine} - \delta^{13}C_{Sample}}{\delta^{13}C_{Marine} - \delta^{13}C_{Terrestrial}}\right) \cdot 100$$

Where $\delta^{13}C_{Sample}$ is equivalent to the value found for a given sample, and $\delta^{13}C_{Terrestrial}$ and $\delta^{13}C_{Marine}$ are the values of the isotopic compositions of the terrestrial and marine sources, respectively. The assumed value for the terrestrial C_3 plants end-member was -31.8 ‰ (Martinelli et al., 2021) and -19.9 ‰ for the marine end-member (Bianchi et al., 2018). Since the possible OM sources for Sinnamary and PSR coastal zones are different, it was necessary to use the model with the respective $\delta^{13}C$ and $\delta^{15}N$ values for each area on the following equation (2):

$$\text{Eq. 2: } C_3 \text{ plants} = \frac{(\delta^{15}N_C - \delta^{15}N_B)\cdot(\delta^{13}C_{Sample} - \delta^{13}C_B) - (\delta^{13}C_C - \delta^{13}C_B)\cdot(\delta^{15}N_{Sample} - \delta^{15}N_B)}{(\delta^{15}N_C - \delta^{15}N_B)\cdot(\delta^{13}C_A - \delta^{13}C_B) - (\delta^{13}C_C - \delta^{13}C_B)\cdot(\delta^{15}N_A - \delta^{15}N_B)}$$

Where $\delta^{13}C_{Sample}$ and $\delta^{15}N_{Sample}$ are the values of the isotopic compositions of the sediment samples. For Sinnamary coastal zone, A, B, and C represent the sources of OM from the terrestrial C_3 plants (mangrove), microphytobenthos (MPB), and marine phytoplankton, respectively. The $\delta^{13}C$ and $\delta^{15}N$ values for the mangrove (*Avicennia germinans* litter) were assumed to be -30.1 ‰ and 2.6 ‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively, and for MPB, the values were -20.9 ‰ and 4.6 ‰ (Ray et al., 2018). The marine source values were -23.9 ‰ and 3.4 ‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively (Matos et al., 2020). Toward the PSR coastal zone, the isotopic compositions of A, B, and C represent the sources: terrestrial C_3 plants, marine phytoplankton, and terrestrial C_4 plants, respectively. The $\delta^{13}C$ and $\delta^{15}N$ values for the terrestrial C_3 plant source were -31.3 ‰ and 2.7 ‰, respectively (Martinelli et al., 2021). For marine phytoplankton, the $\delta^{13}C$ and $\delta^{15}N$ values were -19.0 ‰ and 7.5 ‰ (Gatts et al., 2020), respectively. The isotopic composition values of C and N for terrestrial C_4 plants were -14.6 ‰ (Ribas, 2012) and 7.1 ‰ (internal unpublished data), respectively.

Burial Flux

To estimate the burial flux (F_{burial}) of BC in coastal zones sedimentary compartments the following equation (3) was used (Sánchez-García et al., 2013):

Eq. 3: $F_{burial} = BC \cdot DBD \cdot SAR \cdot (1 - \Phi)$

Where BC is the sum of B5CA and B6CA (µg g^{-1}), DBD is the dry bulk density (g cm^{-3}) and SAR is the sedimentation accumulation rate (cm yr^{-1}). The DBD values were calculated for each sample. SAR values were 1 (Marchand, 2017), 1.5 (Matos et al., 2020), and 0.6 (Wanderley et al., 2014) for the Sinnamary River, Amazon, and PSR coastal zones, respectively. The central porosity value (0.75) commonly applied for global calculations was used (Jönsson et al., 2003).

Statistical Analyses

Statistical analyses were performed with R software (R Core Team, 2018). The descriptive statistics used were median and interquartile ranges. Differences in $\delta^{13}C$ (‰), BC (mg g^{-1} OC), and B6CA:B5CA values between coastal zones were evaluated by ANOVA (*aov*, Base Package, R Core Team, 2018) followed by a multiple comparison test (*TukeyHSD*, base package, R Core Team, 2018), assuming a 95 % confidence level. Pearson's correlation analysis was performed to evaluate the correlation between the parameters (Electrical conductivity, $\delta^{13}C$, BC, and the estimated sources for OM).

Linear regression models were proposed to evaluate the relationship and behavior between $\delta^{13}C$, BC and the condensation degree along the electrical conductivity gradient, which, in turn, was used as a tracer of seawater intrusion (*lm*, ggplot2 Package, Re Core Team, 2018). Additionally, to evaluate the sources for BC content, a linear model was constructed between BC and the contribution of terrestrial C_3 plants (*lm*, ggplot2 Package, Re Core Team, 2018). The assumptions of the linear models (normality, linearity, and homoscedasticity of the residuals) were evaluated using a maximum likelihood function (*boxcox*, MASS package, Venables and Ripley, 2002).

RESULTS

Sources of organic matter in coastal sediments

The $\delta^{13}C$ values of OM from the coastal zone of the PSR were more ^{13}C-enriched (-22.6 ± 1.3 ‰, one-way ANOVA: $F = 6.466$, $p < 0.01$) when compared to those found in the sedimentary compartments of the Sinnamary and Amazon River coastal zones (-25.0 ± 3.1 and -26.1 ± 1.0 ‰, respectively) (Figure 2A; Supplementary Table 2). Along the electrical conductivity gradient, $\delta^{13}C$ values of OM ranged between -27.7 and -25.1 ‰, -32.4 and -20.7 ‰, and -24.8 and -20.4 ‰ for the Sinnamary, Amazon, and PSR coastal zones, respectively, with a tendency towards ^{13}C enrichment with increasing electrical conductivity values (Figure 2B).

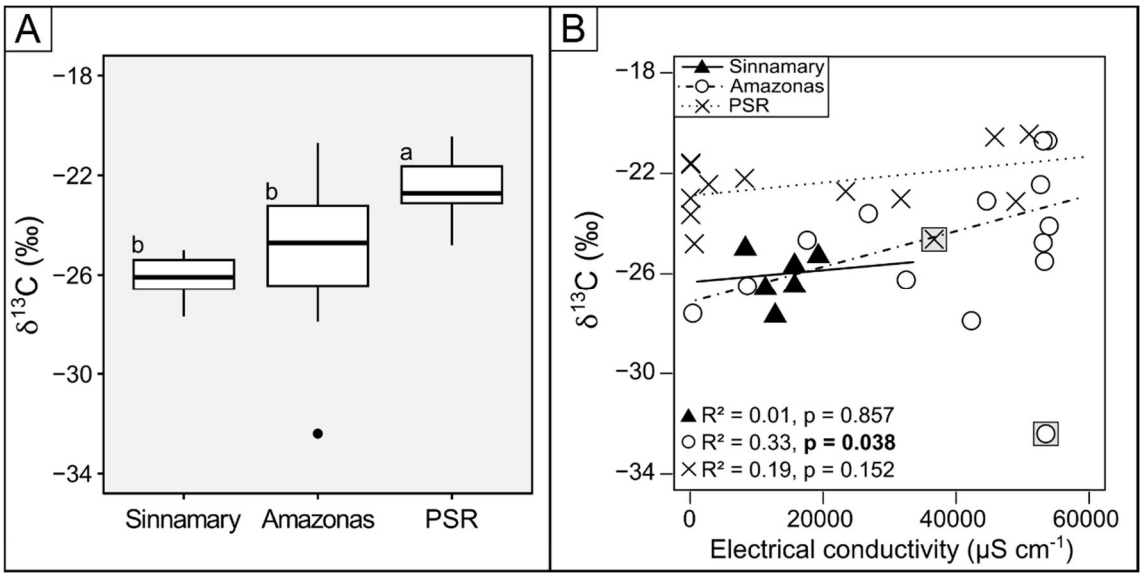

Figure 2. Boxplot representation of $\delta^{13}C$ values (A) and their distribution along the electrical conductivity gradient for the Sinnamary, Amazon, and PSR coastal zones (B). Different letters upon the boxplots represent statistical support for the difference of the mean (Tukey's test, $p < 0.05$) and circles represent outliers (A). Linear regressions of the models were Y = -26.48 + 0.00002 X, Y = -27.14 + 0.00007 X, and Y = -22.89 + 0.00002 X for the Sinnamary, Amazon, and PSR coastal zones, respectively (B). The highlighted symbols were not used in the construction of the models.

The composition of sources of sedimentary organic matter was modeled by the Bayesian stable isotope mixing models. The estimated relative percentages of sources contributing to OM for the Sinnamary River coastal sediments averaged 35, 27, and 37 % for marine sources, MPB, and terrestrial C_3 plants, respectively. For the Amazon coastal sediments, C_3 plants accounted for 49 % of the OM. The contributions for the PSR coastal sediments were 41 % for marine sources, 35 % for C_3 plants, and 24 % for C_4 plants.

BC in coastal zones

The BC content, normalized by OC content, showed similar distribution among the three coastal zones (one-way ANOVA: $F = 2.598$, $p = 0.095$) (Figure 3A). The OC content for the Sinnamary, Amazon, and PSR coastal zones were 0.73 ± 0.68, 0.32 ± 0.24, and 0.95 ± 0.74 mg g^{-1} OC, respectively (Figure 3A; Supplementary Table 2). When considering the electrical conductivity gradient, the BC content showed different distribution for the zones (Figure 3C). For the PSR coastal zone, the content tended to increase with increasing electrical conductivity values, while there was a rapid decrease in content for the Sinnamary coastal zone and little variation in the Amazon coastal zone (Figure 3C). The B6CA:B5CA ratio, used to evaluate the degree of condensation of BC, was higher for the PSR coastal zone sample set (one-way ANOVA: $F = 4.826$, $p < 0.05$) (Figure 3B). The degree of condensation for the Sinnamary, Amazon, and PSR was 0.28 ± 0.17, 0.29 ± 0.23, and 0.50 ± 0.15, respectively (Figure 3B). Similar to BC content, the degree of condensation was different along the electrical conductivity gradient for the coastal zones (Figure 3D). A rapid decrease in the degree of condensation was observed in the Sinnamary coastal zone, while an increase was observed in the Amazon coastal zone and little variation took place in the PSR coastal zone (Figure 3D).

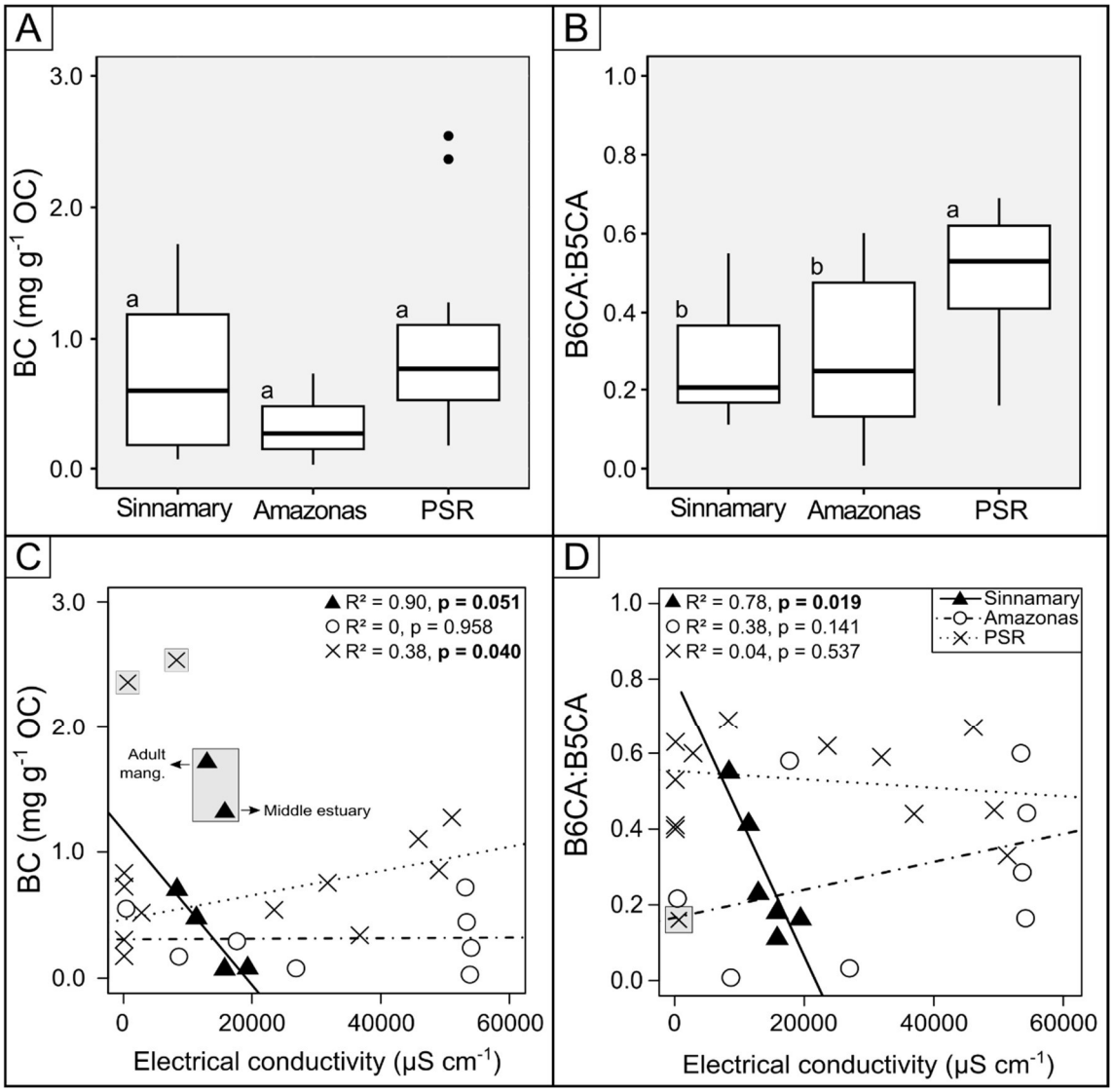

Figure 3. Boxplot representation of BC values normalized by OC content (A) and degree of condensation (B). BC content (C) and degree of condensation (D) along the electrical conductivity gradient in the coastal areas of the Sinnamary, the Amazon, and the PSR. Different letters upon the boxplots represent statistical support for the difference of the mean (Tukey's test, $p < 0.05$) and circles represent outliers (A and B). The linear regressions of the models for BC were Y = 1.17 - 0.00006 X, Y = 0.31 + 0.0000002 X, and Y = 0.47 + 0.00001 X for the Sinnamary, Amazon and PSR coastal zones, respectively (C). Models of the degree of condensation were constructed from the equations: Y = 0.81 - 0.00004 X, Y = 0.05 + 0.0000056 X, and Y = 0.55 - 0.000001 X for the Sinnamary, Amazon, and PSR coastal zones, respectively (D). The highlighted symbols were not used in the construction of the models.

DISCUSSION

Sources of organic matter in coastal sediments

The ^{13}C enrichment of the PSR coastal zone represents a typical signal of terrestrial C_3-C_4 plants mixtures, showing changes in land use in this drainage basin reflecting surface sediments. In the Amazon and Sinnamary, the sedimentary OM has a strong signal from C_3 plants from the local forests (Figure 2A). However, the enrichment of ^{13}C values in the coastal zone sediments indicates a contribution of the marine source for sedimentary OM with increasing electrical conductivity values for the Amazon and PSR (Figure 2B). When evaluating the particulate OC along the continent – ocean gradient of the PSR, Marques (2017) observed ^{13}C-enriched values ranging from -25 to -23 ‰, with C_4 plant contribution ranging from 27 to 40 %. In addition, according to the same author, the variation in $\delta^{13}C$ values in the estuarine samples depends on river discharge, as in events of higher river discharge the author found more ^{13}C depleted values, indicating a stronger contribution from mangroves (terrestrial C_3 plants) present in the estuarine zone during high flow.

By using coupled $\delta^{13}C$ values with the atomic ratio between carbon and nitrogen [$(C:N)_a$] and with $\delta^{15}N$ it is possible to distinguish the proportions of possible OM sources for the sediment samples (Figure 4). There is heterogeneous variation in the sources contributing to the OM of coastal zone surface sediments, with marine sources contributing intensely to some samples from the PSR and the Amazon coastal zones (Figure 4A). According to Ward et al. (2015), about 50 % of continental OM does not reach the coastal zone due to a combination of intense remineralization and the OM sedimentation processes occurring in the Amazon River. In the Amazon River plume, OM continues to be extensively remineralized and terrestrial OM is rapidly replaced by marine OM, which explains the strong enrichment in ^{13}C along the conductivity gradient (Aller and Blair, 2006) (Figure 2B). The relationship between the OM tracers shows that the samples from the Sinnamary coastal zone have a majority contribution of C_3 vegetation, probably a mixture of the mangrove present in the estuary, vegetation debris transported by the river, and freshwater phytoplankton (Figure 4B). When investigating the SPM in the Sinnamary estuary, Ray et al. (2018) observed the same sources for OM and also reported the important contribution of biofilm formed by MPB to the sediment compartment.

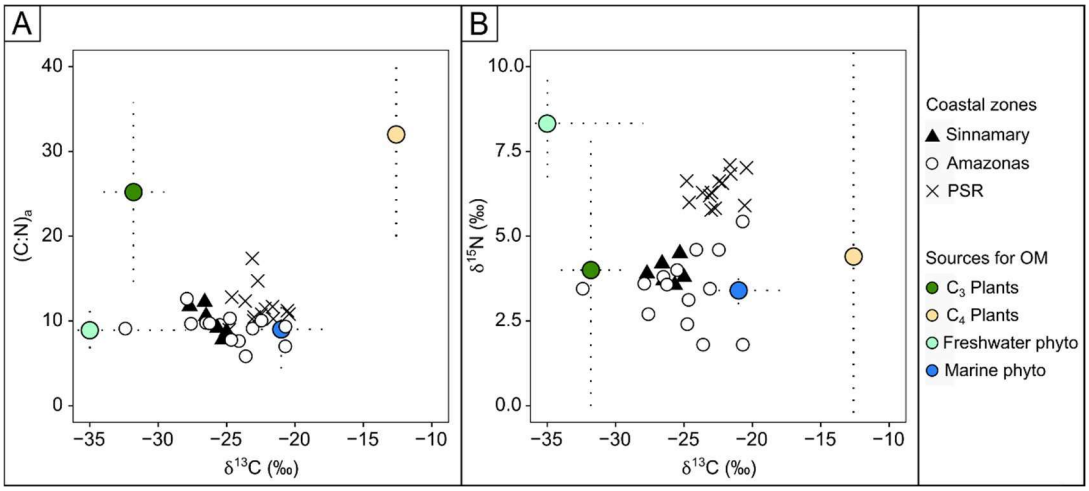

Figure 4. $\delta^{13}C$ *vs.* $(C:N)_a$ (A) and $\delta^{13}C$ *vs.* $\delta^{15}N$ (B) in the coastal zones of the Sinnamary, Amazon, and PSR. End Members sources from Martinelli et al. (2021), Hamilton and Lewis (1992), Bouillon et al. (2011), Ribas (2012), Ellis et al. (2012) and Caraballo et al. (2014) and Ray et al. (2018).

The MixSIAR modeling showed the contribution of potential sources to the OC content in the three coastal zones. Sinnamary coastal zone samples set showed the majority contribution from terrestrial C_3 plants, except for the sample collected near the mangrove pioneer area, in which 55 % of OM sediment was from MPB. Conversely, the surface sediment sample collected in the adult mangrove area showed the lowest contribution of MPB (19 %) and the highest contribution of terrestrial C_3 plants, around 70 %, among the samples collected in the coastal zone of the Sinnamary River. According to Marchand et al. (2003), the decrease in the presence of biofilm formed by MPB occurs with increasing mangrove age, and this explains the strong negative correlation observed between the contributions of terrestrial C_3 plants and MPB to the OC content of the Sinnamary estuary sediment in the present study ($r = -0.92$, $p = 0.009$). The high marine source contribution to the PSR coastal sediments can be attributed to the low discharge of the PSR observed during the sampling period, as a consequence of low precipitation (below 50 % of normal) observed as a result of the La Niña macroclimatic variation (Marques et al., 2017; Costa et al., 2018), and also due to anthropic modifications of the PSR watershed (Carvalho et al., 2002; Souza et al., 2010). A majority of the marine source was also observed on the Amazon samples, the same trend observed by Sun et al. (2017), with $\delta^{13}C$ values enriched in ^{13}C (-18.6 ‰) on the marine surface sediments. Additionally, by analyzing the phenolic products of lignin, the authors also observed that terrestrial OM reaching the area of influence of the

Amazon River plume undergoes extensive diagenetic alteration before it is deposited, as previously observed by Aller and Blair (2006) and Ward et al. (2015).

BC in coastal zones

No statistical differences were observed between the BC content found in the different coastal zones, even though the divergence between the sizes of drainage basins and river discharge (Figure 1, 3A). Similarly, Coppola et al. (2018) also did not observe a statistical difference in the BC contribution to the OC content between the largest rivers worldwide and small rivers. However, the measure of central tendency was relatively lower in the Amazon coastal zone when compared to the Sinnamary and PSR coastal zones. The same trend was observed by Coppola et al. (2018), where BC content contributed to around 14 % of the OC on the largest rivers, and around 18 % for small rivers. The relatively low BC content observed in the coastal zone of the Amazon River can initially be explained by dilution caused by high river discharge (Figure 3A). In addition, the high residence time of particles in river systems with extensive lowlands results in higher remineralization of OM transported along with the river system (Bianchi et al., 2018). As consequence, the BC mainly composed of labile and semi-labile carbon can be degraded and replaced by non-thermally modified OM in floodplains before reaching the coastal zone (Frueh and Lancaster, 2014; Cotrufo et al., 2016). This likely degradation in the fluvial section of the continent – ocean gradient explains not only the low content but also the low variation observed along the electrical conductivity gradient, indicating that the pyrogenic material found in the coastal zone of the Amazon may be composed mainly of stable polycyclic aromatic carbon (Figure 3A and C) (Bird et al., 2015). The heterogeneity in the degree of condensation of the samples along the electrical conductivity gradient indicates that there may be at least two mechanisms acting on the deposition of BC in the sedimentary compartment: the removal of hydrophobic components from the dissolved BC fraction followed by co-precipitation (Coppola et al., 2014), and remobilization of aged BC from alluvial sedimentary deposits (Wagner et al., 2018). On the North Pacific Ocean, in addition to photodegradation controlling the loss of BC in the dissolved fraction of water, adsorption of the highly condensed structures onto particles has also been shown to be an important removal mechanism of BC in marine systems (Nakane et al., 2017). Due to the

energetic margin and high loading of the Amazon River, particles are subject to numerous cycles of deposition and resuspension during lateral transport and, as a consequence, BC can be stocked in intermediate reservoirs before composing the marine sediment compartment (McKee et al., 2004; Coppola et al., 2018). The heterogeneity trend for the degree of condensation found by Sánchez-García et al. (2013) in coastal sediments on the Guadiana plume, also indicated the fluvial transport of aged BC near the coast as an important process for BC deposition in the coastal sediment. Thus, it can be inferred that samples with a low degree of condensation may reflect aged condensed compounds due to intense remineralization along the entire Amazon gradient (Coppola et al., 2014).

Although the measure of central tendency for BC content in sediments from the coastal zones of the Sinnamary River and PSR were similar, they showed different trends along the electrical conductivity gradient (Figure 3A and B). In contrast to the transport of BC along the continent – ocean gradient in the Amazon River, in small to medium-sized rivers, such as the Sinnamary and PSR Rivers, BC reaches the coastal zone more rapidly due to the relatively short time between entry into the aquatic environment and deposition in coastal sediments (Burdige, 2007). In Sinnamary coastal zone, BC appears to be rapidly degraded along the electrical conductivity gradient. Although dilution by SPM transported by the Amazon River plume into the coastal zone of French Guiana seems to explain the low concentrations of inorganic pollutants in the sediment of Sinnamary estuary (Marchand et al., 2006), the decrease in BC content seems to be driven by the dominance of labile and semi-labile aromatic carbon, a trend consistent with the observed decrease in the degree of BC condensation. Unlike stable polycyclic aromatic carbon that can persist in environmental compartments for hundreds of years, the labile and semi-labile components of BC can be remineralized or transformed over timescales of a few years to a few decades (Bird et al., 2015). The highest BC content observed for this zone was in sediments in an adult mangrove channel and the salt wedge. Mangroves have a large capacity to retain allochthonous OM in their sediment compartment from fluvial transport (Chew and Gallagher, 2018). When evaluating the proportion of BC to OC sediment content in mangroves, Chew and Gallagher (2018) found high contributions of BC to OC content and attributed the high concentration to fluvial transport, since mangroves do not burn. Moreover, it is important to emphasize the importance of BC trapping

from soot through the canopy (Agawin and Duarte, 2002). In the salt wedge zone, flocculation and subsequent deposition can facilitate the accumulation of fine particles becoming a site of thermally and non-thermally modified OM deposition (Eisma et al., 1994).

Along the electrical conductivity gradient of the PSR coastal zone, the increased content and stability of the degree of BC condensation highlights the refractory nature of BC for this coastal region. Saiz et al. (2015) observed that in landscapes consisting mainly of grasses, higher production of stable material is observed. Thus, the current BC production in the PSR basin seems to explain the higher degree of BC condensation of the zone and the stability of the thermally modified OM along the electrical conductivity gradient. By using the relation between BC and the contribution of terrestrial C_4 plant, Marques et al. (2017) identified the historical burning of the Atlantic rainforest as the predominant source of dissolved BC in the PSR, as previously suggested by Dittmar et al. (2012), with the degree of condensation ranging between 0.27 and 0.38. The solubilization of BC in soil and its subsequent entry into the aquatic system can take hundreds of years, which seems to explain the results found by the authors. Thus, it is expected that BC from historical burning is removed from soil mainly by the solubilization of soil OM (Dittmar et al., 2012). Changes in vegetation cover and current BC production increase soil erosion (Smith et al., 2011) making the input of recently produced BC into the aquatic system more important for the SPM. When estimating BC content in the particulate and dissolved fractions of water, Wagner et al. (2015) observed an immediate contribution of BC after combustion to the SPM with a decrease each year following the burning event. However, management by fire in pasture and sugarcane areas continues to occur annually in the PSR basin (Ferreira et al., 2021), thereby increasing the pool of BC in soils. Thus, the difference in source and quality between BC in the sediment compartment in the present study and the dissolved fraction (Marques et al., 2017) can be explained by differences in molecular composition modulation for the different water fractions (Wagner et al., 2018).

Sources for BC and burial flux

From the relationship between the contribution of C_3 plants to sedimentary OM and the BC content found from coastal zones, it was possible to infer that the

thermally modified OM of the sediment compartment of each zone tends to vary with the current vegetation cover of each basin (Figure 5). The estimated C_3 plants' contribution does not distinguish vascular plants from the autochthonous production on the rivers, thereby, the determination coefficient exhibited this “mixture” factor. Although the history of Atlantic rainforest burning explains the BC concentrations in the dissolved fraction of water (Marques et al., 2017), the BC content in sediments tends to decrease with increasing terrestrial C_3 source contribution to the OM of the PSR coastal sediment. High BC content (2.37 mg g^{-1} OC) found in a sample where there is no contribution from terrestrial C_4 plants and exhibiting a low degree of condensation may indicate the contribution of old BC from historical burning. Jones et al. (2017) highlight the importance of atmospheric soot deposition for the BC content in the PSR, as recently produced soot (e.g., from biomass or fossil fuel burning) that is not transferred to BC in the dissolved fraction can be transported with the SPM along the river and be deposited. Thus, in addition to being carried via river transport, some of the BC deposited in the coastal zone of the PSR can be transported via the atmosphere. Atmospheric transport into the coastal zones of the Amazon and Sinnamary Rivers does not appear to be important for BC content. According to Coppola et al. (2019), BC from atmospheric deposition is rapidly removed or diluted in the fluvial sector of the Amazon River.

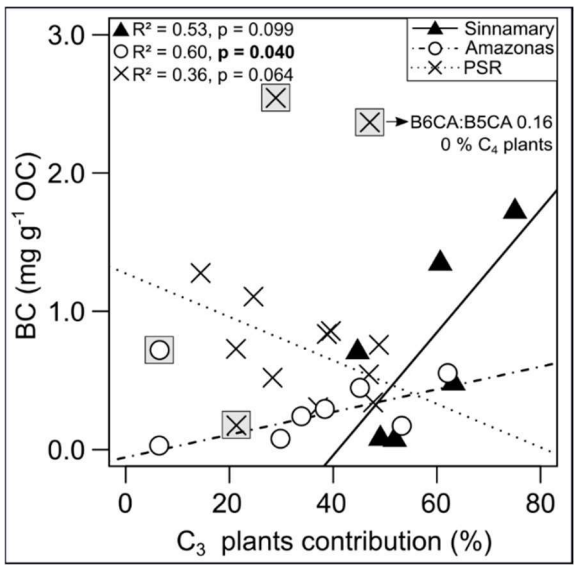

Figure 5. Contribution of terrestrial C_3 plant for the OM vs. BC content to the coastal zones of the Sinnamary, Amazon, and PSR. The linear regressions of the models were Y = -1.818 + 0.004 X, Y = -0.056 + 0.008 X, and Y = 1.274 - 0.016 X for the Sinnamary, Amazon, and PSR coastal zones, respectively. The highlighted symbols were not used in the construction of the models.

Estimates of burial flux for coastal zones are important for better understanding the global budgets of thermally modified OM in coastal sediments since it is their final fate (Sánchez-García et al., 2013). The burial flux of BC content was calculated for the coastal zones and showed mean values of 1.5 ± 1.5, 0.5 ± 0.4, and 2.4 ± 1.5 μg cm^{-2} y^{-1} for the coastal zones of the Sinnamary, Amazon, and PSR Rivers, respectively. Receiving a constant input of BC from the management of cropland and pasture areas that constitute the landscape of the devastated biome, the PSR coastal zone showed a higher burial flux of BC among the study areas. Since there are different techniques for determining BC in different areas of the combustion continuum and different uses of the same technique (e.g., using B3CA and B4CA acids in estimating BC content and/or applying conversion factors [Glaser et al., 1998]), comparisons between different investigations based on different methodologies and data analysis techniques should be performed with caution.

CONCLUSION

By coupling the $\delta^{13}C$ with other OM tracers ($\delta^{15}N$ and $(C:N)_a$) data, it was possible to understand the dynamics of the OM of the coastal zones and estimate the contributions of the sources from the Bayesian model, MixSiar. Also, it made it possible to evaluate if the modification of the vegetation cover of the PSR basin from forest to grass had modified the quality of the OM transported to the coastal ocean. Additionally, we combined the common terrestrial source contribution (terrestrial C_3 plants) and BC content to understand BC production in the drainage basins of the coastal areas of the present study.

PSR set samples exhibited values of the mixture of C_3 and C_4 plants, with more ^{13}C-enriched values, showing that the modification of the Atlantic Rainforest to cropland and pasture areas is changing the OM associated with the particles transported to the coastal zone. Even though the $\delta^{13}C$ analysis was performed on the OC bulk and not on the molecular markers of BC – the BPCA, it is possible to assume that the BC production from the incomplete burning of terrestrial C_4 plant biomass is the main source of BC on the PSR coastal sediments.

The processes that SPM is subject to in the fluvial portion of the Amazon River and the dilution by high material discharge guide the low black carbon content in the coastal zone, but this may change due to the high degree of agricultural speculation in the Amazon fostered by current Brazilian government policies will exacerbate both, social and ecological impacts on the biome. Over the last 14 years, deforestation and forest fire rates in Brazil's Legal Amazon have increased to record levels. Thus, fires from anthropic activities that increasingly remove biomass in the Amazon rainforest can increase the content of BC transported to the coastal zone. Even though the land-use change exhibited a potential to produce more BC dominated by stable aromatic carbon in this study, it is important to consider that the Amazon Rainforest accounts for 93 ± 23 Pg C aboveground, which can substantially increase BC production and have significant impacts on the carbon cycle.

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SUPPLEMENTARY INFORMATION

Supplementary Table 1. Sampling locations (latitude and longitude), electrical conductivity (μS cm^{-1}), carbon and nitrogen isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$, respectively), carbon and nitrogen atomic ratio, black carbon content normalized by organic carbon content and degree of condensation (B6CA:B5CA).

Coastal zone	Latitude	Longitude	Electrical conductivity (μS cm^{-1})	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$(C:N)_a$	BC (mg g^{-1} OC)	Degree of condensation
Sinnamary	5°27'31"N	53°0'24"W	15704	-26.5	3.7	10.61	1.35	0.11
	5°29'9"N	53°0'7"W	19280	-25.3	4.5	7.82	0.08	0.16
	5°28'21"N	53°2'49"W	11314	-26.6	4.2	12.25	0.48	0.41
	5°28'24"N	53°2'16"W	8303	-25.0	3.8	8.76	0.70	0.55
	5°28'23"N	53°2'15"W	12791	-27.7	3.9	11.74	1.72	0.23
	5°27'29"N	53°0'2"W	15704	-25.7	3.6	9.20	0.07	0.18
Amazon	0°10'13"S	47°57'11"W	53300	-25.5	4.0	9.53	0.45	0.29
	0°57'6"N	49°38'52"W	400	-27.6	2.7	9.67	0.55	0.21
	2°5'29"N	47°40'5"W	53800	-20.7	1.8	9.33	0.03	0.16
	0°3'17"N	48°42'22"W	42300	-27.9	3.6	12.62	0.00	0.00
	2°2'3"N	48°49'56"W	8600	-26.5	3.8	9.77	0.17	0.01
	3°33'3"N	50°7'15"W	54000	-24.1	4.6	7.63	0.24	0.44
	1°1'33"N	47°4'1"W	53500	-32.4	3.5	9.10	0.00	0.00
	0°38'39"S	46°46'26"W	44600	-23.1	3.5	9.10	0.00	0.00
	1°39'25"N	48°2'14"W	26800	-23.6	1.8	5.83	0.08	0.03

Continue

Continued

	2°19'15"N	48°37'54"W	53100	-24.8	2.4	10.30	0.00	0.00
	3°56'56"N	47°36'19"W	53100	-20.7	5.4	7.01	0.72	0.60
	3°5'39"N	50°30'28"W	17600	-24.7	3.1	7.77	0.29	0.58
	1°54'35"N	46°38'25"W	52700	-22.5	4.6	10.04	0.00	0.00
	0°34'3"N	47°59'52"W	32500	-26.2	3.6	9.72	0.00	0.00
	21°38'31"S	41°3'23"W	84	-23.6	6.3	12.34	0.84	0.53
	21°36'27"S	40°59'16"W	36700	-24.6	6.0	12.81	0.34	0.44
	21°36'6"S	41°2'47"W	2790	-22.4	6.6	10.81	0.52	0.60
	21°36'59"S	41°1'57"W	88	-21.6	7.1	11.68	0.18	0.41
	21°35'16"S	41°2'55"W	74	-23.0	6.3	10.45	0.31	0.40
	21°34'57"S	41°3'10"W	8200	-22.2	6.6	11.47	2.54	0.69
PSR	21°37'2"S	41°1'20"W	108	-21.6	6.8	10.25	0.73	0.63
	21°35'4"S	41°2'40"W	31700	-23.0	5.8	10.03	0.76	0.59
	21°37'3"S	41°0'15"W	638	-24.8	6.6	8.96	2.37	0.16
	21°36'41"S	40°59'42"W	23400	-22.7	5.8	14.73	0.54	0.62
	21°35'16"S	40°57'12"W	45800	-20.6	5.9	11.21	1.11	0.67
	21°31'50S	40°57'55"W	49000	-23.1	6.2	17.37	0.86	0.45
	21°29'1"S	40°49'42"W	51000	-20.4	7.0	10.82	1.28	0.33

Supplementary Table 2. Isotopic fractionation factors for carbon and nitrogen isotopic compositions used on the MixSIAR model for each coastal zone.

Isotopic fractionation factors			
Coastal Zone	**Source**	**$\delta^{13}C$**	**$\delta^{15}N$**
Sinnamary	Marine	0.915	0.862
	Microphytobenthos	0.800	1.166
	C_3 Plants	1.167	0.735
Amazon	Marine	0.796	0.985
	C_3 Plants	1.271	0.637
PSR	Marine	0.842	1.174
	C_3 Plants	1.385	0.423
	C_4 Plants	0.589	0.250

4. CONSIDERAÇÕES FINAIS

A importância da obtenção de dados acerca do CN em sedimentos costeiros é de extrema relevância devido a sua representação no ciclo global do carbono e sua presença em todos os compartimentos abióticos, que ainda se tem poucos trabalhos publicados.

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