



**UNIVERSIDADE FEDERAL DA BAHIA
INSTITUTO DE GEOCIÊNCIAS
PROGRAMA DE GRADUAÇÃO EM OCEANOGRAFIA**

ANTONI WAL AUGUSTO JATOBÁ JUNIOR

**ESTOQUES DE CARBONO, NITROGÊNIO E MERCÚRIO EM SOLOS DE
MANGUEZAIS SOB DIFERENTES IMPACTOS ANTRÓPICOS**

**SALVADOR
2022**

ANTONI WAL AUGUSTO JATOBÁ JUNIOR

**ESTOQUES DE CARBONO, NITROGÊNIO E MERCÚRIO EM SOLOS DE
MANGUEZAIS SOB DIFERENTES IMPACTOS ANTRÓPICOS**

Este manuscrito representa o trabalho de conclusão do Curso de Graduação em Oceanografia, Instituto de Geociências, Universidade Federal da Bahia, como requisito parcial para obtenção do grau de Bacharel em Oceanografia. Este trabalho é apresentado na forma de um manuscrito que será submetido para uma revista científica.

Orientadora: Profa. Dra. Vanessa Hatje

**SALVADOR
2022**

AGRADECIMENTOS

Primeiramente, a minha mãe, dona Jaque, por fazer o possível e o impossível só pra me ver feliz. Obrigado, mãe, por todo carinho e cuidado, você é a personificação do amor e empatia, te ver, literalmente, chorando de alegria sempre que consegue fazer o bem a quem mais precisa, me faz ser eternamente grato e orgulhoso por ser seu filho. Ao meu querido pai que, antes de partir, foi exemplo de inteligência, honestidade e caráter. Sempre vou guardar em minha memória como você se emocionava quando eu chegava de Salvador pra passar o fim de semana em família, tenho orgulho de ter herdado seu nome, te amo, pai. Aos meus irmãos mais próximos, Matheus, Thiago, Delé e, a mais nova descoberta da family, Biazinha, pelo carinho, bons momentos e, principalmente, por aturarem minhas perturbações, sei que não é fácil. Amo cada um de vocês.

Ao resto da minha família, que me dá um apoio absurdo, Normão (Vovó), Vó lulu, tia Sandra, tia Tate, Rebentão e, especialmente, tia Quíó, que me abrigou nos primeiros semestres do curso. Obrigado aos meus priminhos, Rai, Thai e Lipe pelos bons momentos. A Nana, pelo carinho, principalmente nesse ano tão difícil, você sempre será um pedaço do meu pai aqui na terra.

Aos professores incríveis e toda equipe da UFBA, que fazem o curso de oceanografia INCRIVEL. Obviamente, em especial, agradeço a minha professora e orientadora, Profa. Dra. Vanessa Hatje pelos conselhos, conversas, ensinamentos me mostrando o caminho e esclarecendo todas as minhas dúvidas ao longo do curso, certamente tenho você como minha maior referência e inspiração na oceanografia!

Ao time topper que me ensinou e me ajudou absurdos quando comecei a frequentar o laboratório, Fran, Rai e Manu, sou muito grato pelas conversas, pelo cafezinho e é claro, pelo pãozinho da tarde. Com vocês o CIENAM é incrível.

Aos meus amigos, primeiramente os de longa data, que tenho como irmãos desde que eu me entendo por gente, Sales, Reuna, Wallace, Bruno, Alá e, especialmente, os patetas que moram comigo, Othus, Zé, Danga e Laborda. Agradeço aos grandes BESTOS que foram luz durante a pandemia, Didigo, Vetor, Allan e Beck. Amo todos vocês, obrigado pelos momentos.

Aos colegas que a Oceanografia me presenteou e, hoje, tenho o prazer em chamar de amigos, Ian, George, João Vitor, Juan, Jarbas, Malu, Tamires, Giu, Barbie, Sabrina. Em especial Larinha minha gêmea, minha parceira pra o que eu precisar, Paulinha, parceira de sufoco e minha duplinha no CIENAM e por último, mas não menos importante, meu querido Mauri que é quase

um Co-orientador kkk desse trabalho, muito obrigado por toda ajuda. Cada um de vocês foi essencial para eu chegar onde cheguei.

À FAPESB e ao CnPQ pelo fomento à pesquisa enquanto fui aluno de iniciação científica, o que me ajudou bastante ao longo da minha formação.

Abstract: Mangrove soils are highly efficient in capturing natural and anthropogenic CO₂ and heavy metals, especially Hg which has high affinity with organic matter. However, the soil of mangroves is vulnerable to land use activities, transforming them into a source of C and Hg to the atmosphere. The aim of this study was evaluating the C_{org} stocks and accumulation rates in Brazilian mangrove soils under different degrees of anthropogenic (i.e., sewage discharge and land use activities) influence and evaluate the relationship between C_{org} and Hg in soil. Samples were collected from a mangrove in Paraty (PA) and two others in Florianópolis (Florianópolis Urban (FU) and Florianópolis Pristine (FP)). High dry bulk density values were present in Florianópolis Mangroves ($0.65 \pm 0.30 \text{ g/cm}^3$), indicating possibly soil compaction by land use activities. In Paraty, the $\delta_{15}\text{N}$ ratios were lower ($1.3\text{‰} \pm 2.6\text{‰}$), when compared with the soils from both Florianópolis mangroves ($3.4\text{‰} \pm 1.2\text{‰}$) indicating an increase in microbial activity, and input of high N content from domestic sewage. Moderate correlation between C_{org} and Hg content were observed in Florianópolis mangroves ($r = 0.47$ (FU) and 0.46 (FP)), probably due an input of Hg through atmospheric deposition and sewage effluent discharge which increase the bound between C_{org} and Hg. In Florianópolis Urban, the highest MAR were found in the upper mangrove area ($0.40 \pm 0.07 \text{ g cm}^{-2} \text{ yr}^{-1}$), which indicates that probably some anthropogenic factor started to act around the 2000s and considerably increasing the sediment accesion. Possibly the combination of two or more these factors probably explain the higher contents of C_{org} in Paraty than in mangroves of Florianópolis. Moreover, $d_{13}\text{C}$ and C:N ratios point to different C_{org} input between mangroves. For Paraty mangroves the input of C_{org} seem to be derived principally from C₃ plants and freshwater dissolved organic carbon (DOC). For Florianópolis mangroves in addition C₃ plants input, the $d_{13}\text{C}$ and C:N ratios shows a C_{org} signature from seawater DOC. Although weak, there is evidence of possible anthropic impacts in the accumulation of organic C and Hg.

Keywords: Carbon Stocks, Mangrove, Mercury, anthropogenic impact

Introduction

In the past decade, coastal vegetated ecosystems (mangroves, salt marshes, and seagrass beds) drew the attention of the scientific community due to their important role in climate change mitigation. They have high capacity to store the anthropogenic CO₂ and organic C (C_{org}) storage in soils, as Blue Carbon (Chmura et al., 2003, Laffoley and Grimsditch, 2009, Nellemann et al., 2009). The sustainable management of the Blue Carbon wealth of nations is a key in the ocean-climate nexus providing a nature-based solution that could contribute to the Paris Agreement and the Glasgow Climate Pact (UNFCCC, 2015, 2021).

Among the Blue Carbon ecosystems, mangrove forests present the largest C pool. The mean mangrove global estimate of total C stocks ($856 \pm 64.2 \text{ Mg C ha}^{-1}$) is almost triple that the salt marshes stocks ($317 \pm 38.2 \text{ Mg C ha}^{-1}$) and six-fold seagrass meadows stocks (140 Mg C ha^{-1}) (Kauffman et al., 2020, Alongi, 2018 and Fourqurean et al., 2012, respectively). Those C stock values are high due to the efficient carbon sequestration associated with photosynthesis that promotes C storage in leaves, stems, and branches (aboveground stocks) and the allochthonous land and ocean sediment inputs, that contribute to a high carbon burial rate ($56.6 - 1,073.0 \text{ g C m}^{-2} \text{ year}^{-1}$ Williamson, P., & Gattuso, J. P. 2022) in mangrove soils (belowground stock). Exceeding C_{org} losses from respiration, decomposition, and export due to tidal flux (Ouyang et al., 2017, Alongi, 2014). The slow organic matter decomposition in anoxic mangrove soils favors the storage of soil C_{org} up to millennial times scales (Duarte et al., 2005, Lo Iacono et al., 2008). On the other hand, mangrove soils are vulnerable to land use change due to urbanization, deforestation, and aquaculture, among other activities, which transform rich C_{org} anoxic soils into a C source to the atmosphere (Atwood et al., 2017). Bearing that approximately 85% of C stocks in mangroves are stored belowground, changes in the landscape have an enormous potential to increase greenhouse gas emission to the atmosphere at an average rate of $7.0 \text{ Tg CO}_2 \text{ yr}^{-1}$ (Atwood et al., 2017, Kauffman et al., 2020).

Mangroves provide many other services besides contributions to climate mitigation and adaptation. These services include coastal protection by mitigating erosion and storm surges, food security to coastal inhabitants, nursery grounds for commercial fish, and natural filtering capacity (Alongi 2002; Barbier et al. 2011). During deposition and accumulation of sediments and organic carbon, mangrove soils can also stock excess nutrients and trace metals contaminants discharged by the watershed, anthropic effluents of shrimp farming and sewage, and atmospheric deposition (Marchand et al., 2011, Fitzgerald et al., 2014, Castro et al., 2021). Meantime nutrient-rich waters also can be a problem, because they increase anaerobic microbial activity, modifying mangrove soil redox conditions and thereby affecting negatively soil C storage capacity (Suárez-Abelenda et al., 2013).

Among contaminants, mercury (Hg) has a coupled cycling with C. In soils, where they can be stored on long timescales, they may co-vary closely, especially when complexed with organic matter (Skylberg et al., 2006, Schrumpf, et al., 2013). In addition, mangrove forests grow in fine soils, providing ideal conditions to act as a sink for Hg in soils (Marins et al., 1998, Canário et al., 2003, Marchand et al., 2006, Covelli et al., 2001, Marins, 1997). The presence of mercury, organic matter storage and mobility in soils are strongly influenced by the physical and chemical conditions on a small scale of this matrix and often also related to other factors that influence C, such as atmospheric deposition, soil clay content, and soil drainage regime or annual precipitation (Obrist et al., 2011; Richardson et al., 2013).

Carbon and Hg play different roles in ecosystem dynamics, but they are closely linked in soils and pervasive problems from atmospheric pollution to public health (Nave et al., 2019). Their connection suggests an integrated approach to their study.

Since Brazil is one of the countries with the largest mangrove extent in the world (9200 km; Diniz et al 2019), we have an unexploited hotspot in Brazil's backyards to develop science and understand the role of the mangrove in C uptake and climate change mitigation. Our main goal

here is to evaluate the Corg stocks and accumulation rates in Brazilian mangrove soils under different degrees of anthropogenic influence to contribute to closing this data gap previously identified in the literature (Hatje et al., in review), besides, we also aim to evaluate the relationship between Corg and Hg in bulk soils across the studied ecosystems.

Methods

Sample collection and analysis

Soil cores were collected in November and December 2021. The sampling design included the collection of mangrove soil cores in 3 different environmental conditions (i.e., treatments) (Fig. 1; Table S1). The first area is located in the Paraty-Mirim National Park, Rio de Janeiro, South Brazil (PA; 23°18'S, 44°38'W), an environmental preservation area in Paraty (hereafter called PA) inhabited by traditional communities, where fishing and tourism are the main activities (Villard, 2017; TCERJ, 2021). The other two sites were near urban regions: (i) a very dense mangrove shrub next to residences and a sewage output in Florianópolis, Santa Catarina, South Brazil (FU; 27°39'04.4"S 48°39'42.4"W) (hereafter called Florianópolis Urban-FU); and (ii) a site in a military reserve area with restricted access, also in Florianópolis (27°39'40.9"S 48°33'37.3"W), but potentially impacted from waters coming from the South Bay of Florianópolis (Baía Sul) (hereafter called Florianópolis Pristine, FP). We collected 3 soil cores at each site, i.e., at the lower (fringe), middle and upper (interior) mangrove areas (Table S1). Soil cores were sampled using a stainless-steel open-faced auger up to 100 cm. The depth of the cores varied from 50 cm to 100 cm. All cores were sliced into 2cm-thick layers throughout the first 50 cm and at 5 cm-thick layers till the bottom.

Soil slices were weighed wet, freeze-dried, and weighed again. Soil dry bulk density (DBD) was then determined by dividing the dry weight by the wet sample volume. The sediment grain size was determined with a laser particle diffractometer (Cilas model 1064, France), following

treatment with HCl and H₂O₂. Soils were classified as sand (>63 μm) and fine particles (i.e., the sum of clay and silt; < 63 μm).

C_{org}, total nitrogen (TN), and stable isotope analyses (δ¹³C_{org} and δ¹⁵N) were performed in the bulk fraction of the soils (i.e., no grain size separation). Samples were acidified with 1 M HCl to remove inorganic carbon and to determine the contents of Ca. The C_{org}, TN, δ¹³C_{org} and δ¹⁵N were determined using an elemental analyzer coupled with a Delta V Isotope Ratio Mass Spectrometer (Thermo Fisher, USA).

Concentrations of ²¹⁰Pb were determined through the analysis of its decay product ²¹⁰Po by alpha spectrometry after the addition of ²⁰⁹Po as an internal tracer and microwave-assisted acid digestion (Sanchez-Cabeza et al., 1998). The concentrations of excess ²¹⁰Pb (²¹⁰Pb_{ex}) used to obtain the age models were determined as the difference between total ²¹⁰Pb and ²²⁶Ra (supported ²¹⁰Pb), which was determined for selected samples along each core by low-background liquid scintillation counting (Masqué et al., 2002). These concentrations were confirmed with measurements by gamma spectrometry and found to agree with the concentrations of total ²¹⁰Pb at depths below the excess ²¹⁰Pb horizons in each core. The Constant Flux: Constant Sedimentation (CF: CS) model (Krishnaswamy et al., 1971) was used to calculate the sediment accumulation rates (SAR) and mass accumulation rates (MAR).

The concentration of Hg in soil was determined using an automated analysis system (CV-AFS, Tekran 2600). Samples (0.5g of sediment) were digested with 8mL of an acid mixture (3 HCl 37%: 1 HNO₃ 65% and KMnO₄ (5%)) in a microwave (Mars Xpress Microwave, CEM) for 25 minutes (10 min, until reaching 95 °C and 15 min, at a constant temperature of 95 °C with 1600 W of power).

Data analysis

None of the studied variables (i.e., DBD, Fine sediments, Carbon, Nitrogen, C: N ratio, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and Carbonate) presented normal distribution. To assess the difference between variables for each treatment, the Kruskal-Wallis test was applied, followed by Dun's test. All statistical analyses were performed using the Graph Pad Prism.

We used multivariate principal component analysis (PCA) to assess the relationships between soil properties in the three studied mangroves. The fine fraction of soils, carbonate, C_{org} , and N content, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ signals, Carbon: Nitrogen ratio (C: N), DBD and Hg concentration, were inputted as quantitative variables and the treatments as a qualitative variable. The PCA was performed using the R packages FactoMiner and Factoextra and all quantitative variables were scaled to unit variance.

Results

Significant differences existed between the mangrove soil characteristics (Table S3) of treatments for almost all the studied variables (i.e., DBD, C_{org} , TN and carbonate contents and stable isotope) (Table S3). The PCA nevertheless did not clearly clustered soils by treatments under different level of anthropogenic impact (Fig. 2) but rather having high or low DBD, C_{org} and TN content. The first two principal components (PC1 and PC2) accounted for 58% of the total data variance among sampled soils. The PC1 comprised 42% of the total variance and was strongly correlated with C_{org} ($r = 0.92$), TN ($r = 0.90$) and $\delta^{13}\text{C}$ ($r = -0.82$), and moderately correlated with DBD ($r = -0.67$). The PC2 explained 16% of the total data variance, and was moderately correlated with carbonate ($r = 0.63$), Hg concentration ($r = -0.65$) and $\delta^{15}\text{N}$ ($r = -0.60$).

Soil physico-chemical properties

There were significant differences in DBD (Table S2) between treatments, which ranged from

0.09 up to 1.77 g/cm³ (Parati < Florianópolis Urban < Florianópolis Pristine; $p < 0.05$; Table S3). The DBD values were lower and mostly vertically homogeneous for the three cores at PA (Fig. 3). At FU, the DBD decreased gradually from bottom to surface. The same was observed at FP, although with quite some variability along and between the cores (Fig. 3). Soils were composed mainly by fine particles (i.e., silt + clay > 75%), except by the soils at the lower FP mangrove area (Fig. 3). No significant variability was observed between treatments ($p > 0.05$) in terms of soil granulometry. In PA, the fine fraction was as homogenous as for the DBD. The FU presented the highest mean fine fraction (> 90%) and a slight increase from the bottom to surface, particularly in the upper mangrove area (Fig. 3). At the FP, the granulometry between studied sites was heterogenous and vertically variable. The C_{org}, TN and carbonate content varied significantly between treatments (Fig. 3 and 4; Table S2 and S3). The C_{org}, TN and carbonate content in PA mangrove soils were the highest and ranged from 4.9 to 14.8%, from 0.26 to 0.88% and from 0.8 to 14.2%, respectively, followed by soils in the FU mangrove, with values ranging from 2.55 to 13.1%, from 0.09 to 0.76% and from 0.1 to 7.4% respectively. The lowest values for C_{org}, TN and carbonate were present in mangrove soils in FP; values ranged from 1.2 to 10.7%, from 0.1 to 0.56% and from 0.1 to 7.4%, respectively. The mean values for C_{org} and TN (Table S2) tended to be higher in the upper mangrove soils of PA and FP treatments and in the middle mangrove area for FU. The lowest mean values for C_{org} occurred in the lower mangrove area in PA and FP (9.84 ± 1.37 % and 3.31 ± 0.85 %, respectively) (Table S2) and in upper mangrove area for FU (7.98 ± 3.20 %) (Table S2). The lower mangrove area showed the lowest mean values for N in Florianópolis mangroves (0.44 ± 0.20 % and 0.18 ± 0.06 % for FU and FP, respectively), for PA the lowest N value occurred in middle mangrove area (0.48 ± 0.16 %) (Table S2). No clear intertidal pattern was observed for the carbonate contents.

Through the PA soil profiles (Fig. 4), the C_{org} content presented a slight increase from the bottom to the top, up to ~20cm, after it presented a complex pattern up to surface. The C_{org} and TN content (Fig. 4) increased steadily from the bottom to surface in FU. At the FP, the C_{org} soil profiles differed in content and distribution pattern among cores. The upper mangrove core displayed the lowest concentrations at the bottom which increased towards the surface up to 20 cm despite the variability, while the other two cores, the C_{org} content remained relatively constant. The TN for FP and PA were relatively homogeneous along the cores, with a slight increase in concentrations towards the surface of the cores. The mean C: N molar ratios varied within a narrow interval from 21 ± 3.1 to 25 ± 0.9 (Table S3) and no significant differences were observed between treatments (Table S2).

In PA, the carbonate content tended to decrease towards the surface of the core, with very variability at the top 20 cm of soil. For FU and FP, the carbonate contents were lower than at PA, and more homogeneous along the cores and between studied sites.

For all treatments, the $\delta^{13}C$ content ranged between -27.5‰ and -20.3‰. The mean value for $\delta^{13}C$ was quite similar for PA ($-25.7‰ \pm 0.8‰$) and FU ($-25.1‰ \pm 1.2‰$), but it was significantly higher ($p < 0.05$) for the FP mangrove ($-23.62‰ \pm 1.0‰$). For the upper and middle cores at PA, the $\delta^{13}C$ remained constant at the bottom, but decreased after 18-20 cm up to surface. No vertical variation in the $\delta^{13}C$ was observed for the lower mangrove area. For the FU, the $\delta^{13}C$ signal decreased from the bottom towards the surface up to ~19cm, after that it keeps constant up to the surface. The $\delta^{13}C$ in FP similarly to FU also presented a decreasing trend from the bottom up to ~20 cm, followed by an constant trend.

The $\delta^{15}N$ content for the treatments in Florianopolis showed similar mean values (i.e., 3.1‰ to 3.7‰). At FU, the $\delta^{15}N$ content, for the upper mangrove area remained constant at the bottom followed by an increase towards the surface between 30 and 20 cm, after that, a quickly and punctual decrease in $\delta^{15}N$ content were observed following constant till the surface (Fig. 3).

At the middle mangrove area in FU a slight enrichment in $\delta^{15}\text{N}$ contents was observed from the bottom to the surface, despite a little variability in the first 20cm of the core. For the lower mangrove area, the $\delta^{15}\text{N}$ signal increased gradually towards the surface up to 4.9‰ at 17cm, then decrease until the surface. At the FP soils, the $\delta^{15}\text{N}$ concentrations remained constant at middle and lower mangrove area at the first 25cm, followed by a slight decrease towards the bottom. The upper mangrove core presented high variability (0.4 to 3.3‰) at the top 15cm, followed by a homogenous trend and a slight increase below the 37cm towards the bottom. The $\delta^{15}\text{N}$ values at Parati showed significant difference ($p < 0.05$) from other treatments, presenting the lowest mean value ($1.3\text{‰} \pm 2.6\text{‰}$). At this treatment, there was a high variability between cores that presented a peak in $\delta^{15}\text{N}$ at the 7cm, followed by a sharp decrease and a gradual increase towards the bottom.

Mean mercury concentrations varied from 20.8 ± 3.71 and 41.1 ± 21.7 ng/g (Fig. 3; Table S2). In Parati, Hg concentration along cores, presented high variability (10.4 to 54.9 ng/g) and a complex pattern with an increasing trend towards the surface. The lower mangrove soils presented the highest Hg concentrations. All three mangrove soil cores at FU showed an increase in Hg concentrations from bottom, reaching maximum values between 10 and 20 cm, followed by a decrease in concentrations towards the top layers. The peak area was more pronounced for the lower (46.5 to 67.7 ng/g) and middle mangrove areas (38.1 to 71.5 ng/g). In the FP, Hg concentrations were significantly lower than in the other treatments (22.9 ± 5.7 ng/g; $p < 0.05$) and mostly homogeneous through the core.

^{210}Pb

In all mangrove soils, the total ^{210}Pb activity decreased from the surface (42-170 Bq kg^{-1}) to reaching a constant value compatible with the concentrations of supported ^{210}Pb at depths between 18 and 90 cm (Fig. 5). The CF:CS model was used to estimate the average

sedimentation in good agreement with the results obtained using the CRS model (Krishnaswamy et al. 1971). Mass accumulation rates ranged (MAR) (Table 1) between $0.036 \pm 0.002 \text{ g cm}^{-2} \text{ yr}^{-1}$ and $0.209 \pm 0.007 \text{ g cm}^{-2} \text{ yr}^{-1}$ (or $1.92 \pm 0.10 \text{ mm yr}^{-1}$ and $10.5 \pm 0.3 \text{ mm yr}^{-1}$). No clear pattern could be identified along the intertidal gradient of studied mangroves.

Table 1: Mass and sediment accumulation rates (MAR and SAR, respectively).

Core ID	Length	MAR	SAR	Period
	cm	$\text{g cm}^{-2} \text{ yr}^{-1}$	mm yr^{-1}	covered
Parati				
Upper	85	0.036 ± 0.002	1.92 ± 0.10	Last century
Middle	70	0.039 ± 0.002	1.40 ± 0.08	Last century
Lower	90	0.209 ± 0.007	10.5 ± 0.3	1980- present
		0.138 ± 0.007	7.0 ± 0.4	Before 1980
Florianópolis				
Urban				
Upper	95	0.40 ± 0.07	12 ± 3	2000-present
		0.30 ± 0.06	3.9 ± 0.8	Before 2000
Middle	60	0.150 ± 0.008	4.3 ± 0.2	Last century

Lower	52	0.067 ± 0.008	1.8 ± 0.2	Last century
-------	----	-------------------	---------------	--------------

Florianópolis

Pristine

Upper	70	0.144 ± 0.006	2.79 ± 0.11	Last century
Middle	100	0.137 ± 0.008	1.88 ± 0.11	Last decades
Lower	65	0.178 ± 0.015	2.11 ± 0.18	

Discussion

The mangrove ecosystems addressed in this study presented some variability in soil geochemical properties (i.e., C_{org} , TN, stable isotopes, carbonate, Hg and sedimentation rates) between and within them. This variability is due to a series of factors discussed in literature (Santos-Andrade et al., 2021, Hatje et al., 2021, Castro et al., 2021, Suárez-Abelenda et al., 2013) and observed in studied area, such as intertidal variability, mineral and organic input, biological activity, inputs from wastewater effluents and atmospheric deposition, and land use activities. However, despite the differences observed among treatments, the soil characteristics from these mangroves did not display strong evidences of anthropogenic impact.

In PA, the DBD was lower and richer in fine particles (Table S2) than those observed in other mangroves in Brazil with no human disturbances (0.38 ± 0.07 and 84 ± 4 respectively; Hatje et al. 2021). However, the same did not occur in FU, which displayed the highest fine soil content among the treatments and double DBD (Table S2) in comparison with PA soils. Therefore, it may have occurred soil compaction due to changes in landscape related (Santos-Andrade et al., 2021, Arifanti et al., 2019), for instance, to civil construction, since the mangrove is located close to residences. The FP mangrove, presented the highest DBD values that are probably

linked to the granulometric composition of the mangrove soil, especially in the fringe mangrove which differently from the others sites, and displayed a sandy soil.

In PA, the $\delta^{15}\text{N}$ ratios were significant lower and less than half, when compared with the soils from Florianópolis mangroves. Probably due an increase in microbial activity, with preferential use of the ^{14}N (Heaton, 1986) and also associated with the input of high N content and $\delta^{15}\text{N}$ signal from domestic sewage (Lovelock et al., 2009; Zhou et al., 2014). On the other hand, TN content in PA were slightly higher than in FU and twice as much than in FP. This contrasts what was proposed by Zhou et al., 2014, that normally high values of $\delta^{15}\text{N}$ are often associated with high values of TN and what were observed in impacted mangrove soils by sewage discharge in Santos-Andrade (2021).

The $\delta^{13}\text{C}$ and C:N ratios in PA and FU were quite similar and considerable higher when compared with mangrove soils $\delta^{13}\text{C}$ values (Kristensen et al. 2008). For FP $\delta^{13}\text{C}$ values were even higher and C:N ratios were lowest. In PA these lower $\delta^{13}\text{C}$ signal are, probably, due to inputs from C_3 terrestrial plants and freshwater dissolved organic carbon (DOC) discharge. For Florianópolis mangroves, in addition of input from C_3 terrestrial plants, also marine DOC inputs were displayed according with Lamb et al. (2006).

The C_{org} content for the mangroves observed in PA, FU, and FP were five, four and two-fold, respectively, higher than the estimated global mean C_{org} content ($\sim 2.2\%$; Kristensen et al. 2008). These considerable highly C_{org} values in PA and FU, are possibly due the MAR which varied by an order of magnitude between intertidal zones (Table 1). In PA, the MAR were the highest at the fringe mangrove area probably due to greater vegetation cover and a more extensive root system compared to the rest of the intertidal area. In addition, the fringe mangrove area is more frequently exposed to tidal inundation and inputs from mineral and organic sediments (Hatje et al. 2021). However, in FU, the highest MAR were in the upper part of the mangrove area, that is, in the most distal portion of the water and the closest to the urban

environment, which indicates that probably some anthropogenic factor started to act around the 2000s and considerably increasing the MAR. In FU the MAR were less expressive varying from 1.88 ± 0.11 to 2.79 ± 0.11 , which, together with the low granulometry, in the fringe area of the mangrove, explain why this region presented the lowest C_{org} content.

Mercury concentrations were generally low. Moderate correlation between C_{org} and Hg content were observed in Florianópolis mangrove soils ($r = 0.47$ and 0.46) and lower correlation in PA soils ($r = 0.14$) (Figure 6). The higher correlation between C_{org} and Hg in FU mangroves may be possibly explained by the input of Hg through atmospheric deposition and sewage effluent which also enhance sediment capacity to accumulate organic matter-bound Hg due to an increasing DOC input. Because of this, the highest value for Hg content were present in FU. However, FP which is in relatively close to FU presented the lowest Hg content, probably due to the lowest C_{org} content especially in lower mangrove area. And finally, PA which showed a considerable Hg content, which, in contrast to FP, is probably due to the high content of C_{org} in sediment.

Conclusion

Our results show that the mangroves evaluated in this study are different among them, mostly in terms of C_{org}, TN, DBD, fines, stable isotopes and MAR. Although weak, there is evidence of possible anthropic impacts in the accumulation of organic C and Hg. Moreover, this study helps to fill in gaps present in the literature about Brazilian mangroves, contributing to the greater objective of supporting decision-making regarding the best ways to take advantage of the mangroves to mitigate global warming.

References

- Alongi, D. M. (2018). Seagrass meadows. In *Blue Carbon* (pp. 37-51). Springer, Cham.
- Alongi, D. M. 2002. Present state and future of the world's mangrove forests. *Environ.*
- Alongi, D. M., & Mukhopadhyay, S. K. (2015). Contribution of mangroves to coastal carbon cycling in low latitude seas. *Agricultural and Forest Meteorology*, 213, 266-272.
- Arifanti, V. B., Kauffman, J. B., Hadriyanto, D., Murdiyarso, D., & Diana, R. (2019). Carbon dynamics and land use carbon footprints in mangrove-converted aquaculture: The case of the Mahakam Delta, Indonesia. *Forest Ecology and Management*, 432, 17-29.
- Atwood, T. B., Connolly, R. M., Almahasheer, H., Carnell, P. E., Duarte, C. M., Ewers Lewis, C. J., ... & Lovelock, C. E. (2017). Global patterns in mangrove soil carbon stocks and losses. *Nature Climate Change*, 7(7), 523-528.
- Barbier, E. B., Hacker, S. D., Kennedy, C., Koch, E. W., Stier, A. C., & Silliman, B. R. (2011). The value of estuarine and coastal ecosystem services. *Ecological monographs*, 81(2), 169-193.
- Castro, S., Luiz-Silva, W., Machado, W., & Valezio, E. (2021). Mangrove sediments as long-term mercury sinks: Evidence from millennial to decadal time scales. *Marine Pollution Bulletin*, 173, 113031.
- Chmura, G. L., Anisfeld, S. C., Cahoon, D. R., & Lynch, J. C. (2003). Global carbon sequestration in tidal, saline wetland soils. *Global biogeochemical cycles*, 17(4).

- Diniz, C., Cortinhas, L., Nerino, G., Rodrigues, J., Sadeck, L., Adami, M., & Souza-Filho, P. W. M. (2019). Brazilian mangrove status: Three
- Duarte, C. M., Middelburg, J. J., & Caraco, N. (2005). Major role of marine vegetation on the oceanic carbon cycle. *Biogeosciences*, 2(1), 1-8.
- Fitzgerald, W. F., & Lamborg, C. H. (2003). Geochemistry of mercury in the environment. *Treatise on geochemistry*, 9, 612.
- Fourqurean, J. W., Duarte, C. M., Kennedy, H., Marbà, N., Holmer, M., Mateo, M. A., ... & Serrano, O. (2012). Seagrass ecosystems as a globally significant carbon stock. *Nature geoscience*, 5(7), 505-509.
- Hatje, V., Masqué, P., Patire, V. F., Dórea, A., & Barros, F. (2021). Blue carbon stocks, accumulation rates, and associated spatial variability in Brazilian mangroves. *Limnology and Oceanography*, 66(2), 321-334.
- Heaton, T. H. (1986). Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chemical Geology: Isotope Ge*
- Kauffman, J. B., Adame, M. F., Arifanti, V. B., Schile-Beers, L. M., Bernardino, A. F., Bhomia, R. K., ... & Hernández Trejo, H. (2020). Total ecosystem carbon stocks of mangroves across broad global environmental and physical gradients. *Ecological Monographs*, 90(2), e01405.
- Krishnaswamy, S., Lal, D., Martin, J. M., & Meybeck, M. (1971). Geochronology of lake sediments. *Earth and Planetary Science Letters*, 11(1-5), 407-414.
- Kristensen, E., S. Bouillon, T. Dittmar, and C. Marchand. 2008. Organic carbon dynamics in mangrove ecosystems: A review. *Aquat. Bot.* 89: 201–219.
- Laffoley, D., & Grimsditch, G. D. (Eds.). (2009). *The management of natural coastal carbon sinks*. Iucn.
- Lei, Z. H. O. U., Ming-Hua, S. O. N. G., Shao-Qiang, W. A. N. G., Jiang-Wen, F. A. N., Ji-Yuan, L. I. U., ZHONG, H. P., ... & Ting, S. O. N. G. (2014). Patterns of soil 15N and total N and their relationships with environmental factors on the Qinghai-Tibetan Plateau. *Pedosphere*, 24(2), 232-242.

Lo Iacono, C., Mateo, M. A., Gracia, E., Guasch, L., Carbonell, R., Serrano, L., ... & Danobeitia, J. (2008). Very high-resolution seismo-acoustic imaging of seagrass meadows (Mediterranean Sea): Implications for carbon sink estimates. *Geophysical Research Letters*, 35(18).

Lovelock, C. E., Ball, M. C., Martin, K. C., & C. Feller, I. (2009). Nutrient enrichment increases mortality of mangroves. *PloS one*, 4(5), e5600.

Marchand, C., Lallier-Vergès, E., & Allenbach, M. (2011). Redox conditions and heavy metals distribution in mangrove forests receiving effluents from shrimp farms (Teremba Bay, New Caledonia). *Journal of Soils and Sediments*, 11(3), 529-541.

Masqué, P., Sanchez-Cabeza, J. A., Bruach, J. M., Palacios, E., & Canals, M. (2002). Balance and residence times of ²¹⁰Pb and ²¹⁰Po in surface waters of the northwestern Mediterranean Sea. *Continental Shelf Research*, 22(15), 2127-2146.

Nave, L. E., Covarrubias Ornelas, A., Drevnick, P. E., Gallo, A., Hatten, J. A., Heckman, K. A., ... & Swanston, C. W. (2019). Carbon–mercury interactions in spodosols assessed through density fractionation, radiocarbon analysis, and soil survey information. *Soil Science Society of America Journal*, 83(1), 190-202.

Nellemann, C., & Corcoran, E. (Eds.). (2009). *Blue carbon: the role of healthy oceans in binding carbon: a rapid response assessment*. UNEP/Earthprint.

Ouyang, X., S. Y. Lee, and R. M. Connolly. 2017. The role of root decomposition in global mangrove and saltmarsh carbon budgets. *Earth-Science Rev.* 166: 53–63. doi:10.1016/j.earscirev.2017.01.004

Richardson, J.B., A.J. Friedland, T.R. Engerbretson, J.M. Kaste, and B.P. Jackson. 2013. Spatial and vertical distribution of mercury in upland forest soils across the northeastern United States. *Environ. Pollut.* 182:127–134. doi:10.1016/j.envpol.2013.07.011

Sanchez-Cabeza, J. A., Masqué, P., & Ani-Ragolta, I. (1998). ²¹⁰Pb and ²¹⁰Po analysis in sediments and soils by microwave acid digestion. *Journal of Radioanalytical and Nuclear Chemistry*, 227(1-2), 19-22.

Santos-Andrade, M., Hatje, V., Arias-Ortiz, A., Patire, V. F., & da Silva, L. A. (2021). Human disturbance drives loss of soil organic matter and changes its stability and sources in mangroves. *Environmental Research*, 202, 111663.

Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I., & Schulze, E. D. (2013). Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and attachment to minerals. *Biogeosciences*, *10*(3), 1675-1691.

Skylberg, U., Bloom, P. R., Qian, J., Lin, C. M., & Bleam, W. F. (2006). Complexation of mercury (II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. *Environmental science & technology*, *40*(13), 4174-4180.

UNFCCC (2015). *Adoption of The Paris Agreement FCCC/CP/2015/L.9/Rev.1*. United Nations Framework Convention on Climate Change. Available online at: <http://unfccc.int/resource/docs/2015/cop21/eng/109r01.pdf> (accessed December 14, 2021).

UNFCCC (2021). *Glasgow Climate Pact. Decision -/CP.26*. United Nations Framework. Available online at: https://unfccc.int/sites/default/files/resource/cop26_auv_2f_cover_decision.pdf (accessed December 14, 2021).

Villardí, V. R. (2017). Variabilidade espacial do estoque de carbono nos manguezais da Baía da Ilha Grande (RJ).

Williamson, P., & Gattuso, J. P. (2022). Carbon removal using coastal blue carbon ecosystems is uncertain and unreliable, with questionable climatic cost-effectiveness. *Frontiers in Climate*, *4*.

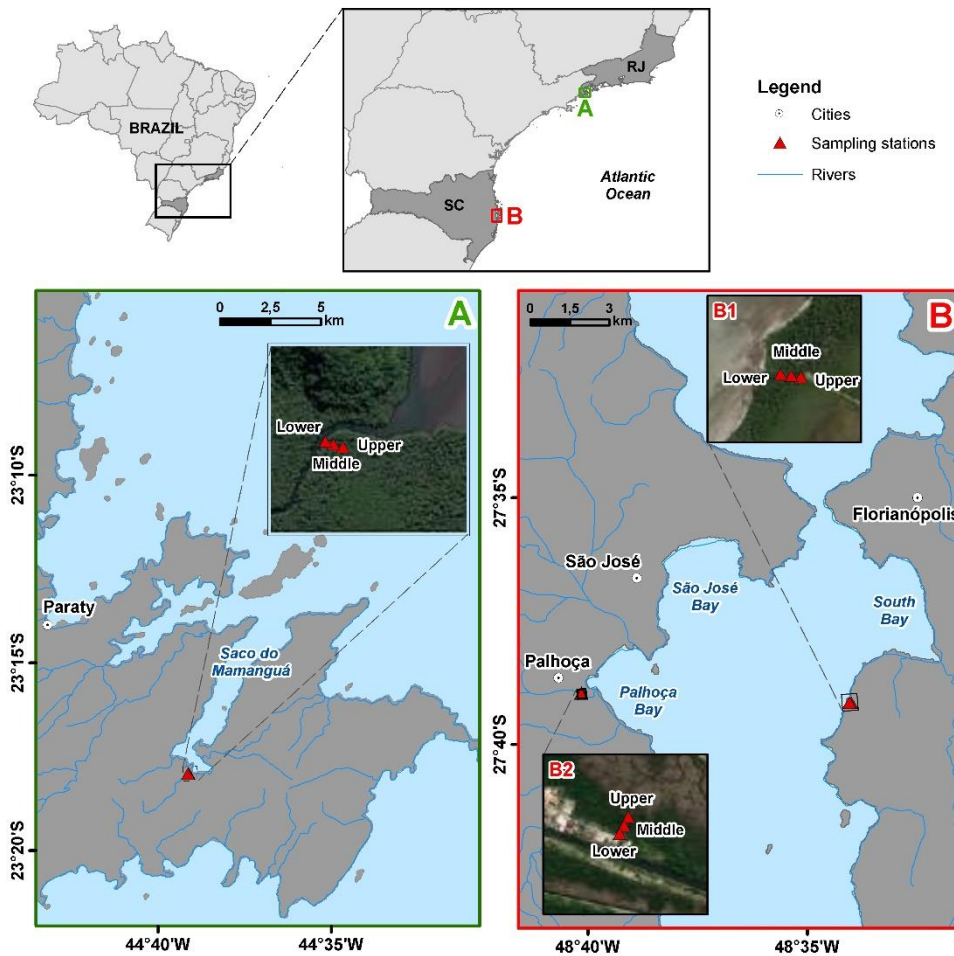


Fig.1 – Study area showing the location where the cores were collected, Paraty (Panel A) and Florianópolis Pristine (Panel B1) and Florianópolis Urban (Panel B2).

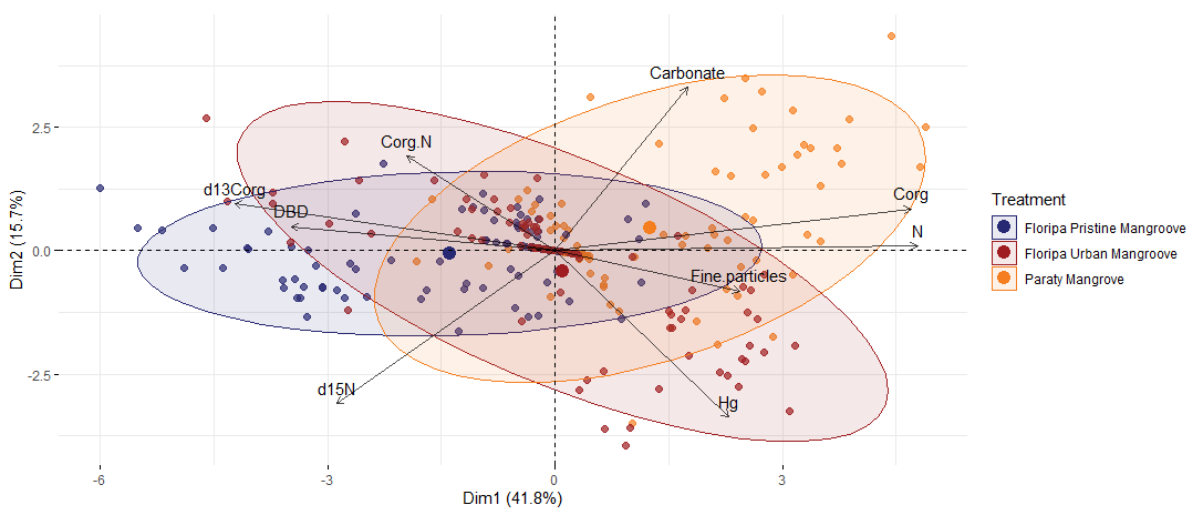


Fig. 2 – Principal component analysis of soil properties (fine particle fraction, Corg, N, Corg:N ratio, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, carbonate, dry bulk density and Hg content) for Paraty, Florianópolis

Urban and Florianópolis Pristine. Superimposed on the plot are the confidence ellipses for each treatment. Group mean points are represented by large circles.

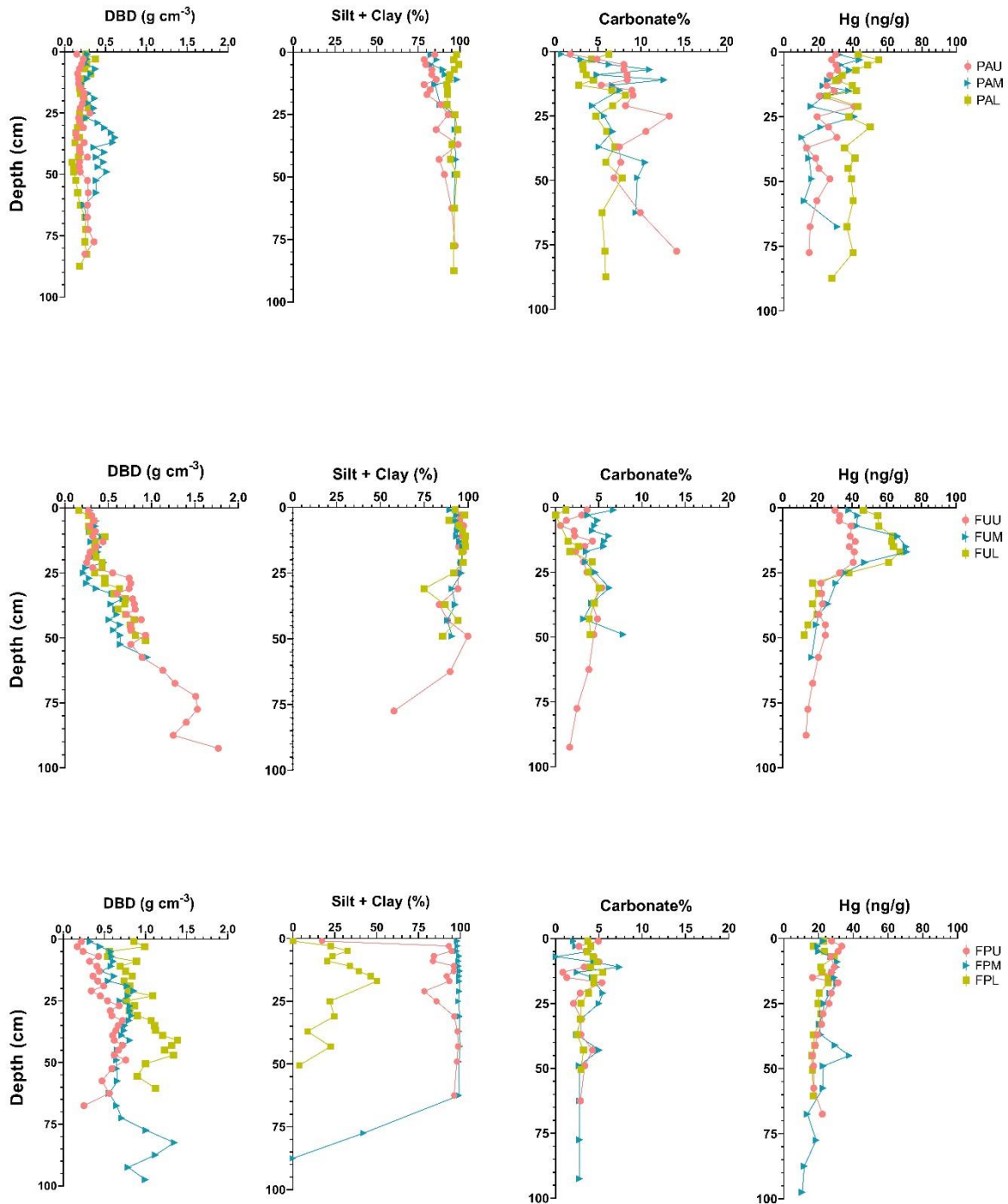


Fig. 3 – Vertical profiles of DBD, grain size, carbonate contents, and Hg concentrations in soils collected at the upper (U), middle (M), and lower (L) regions of Parati (PA), Florianópolis Urban (FU) and Florianópolis Pristine (FP) mangrove soils.

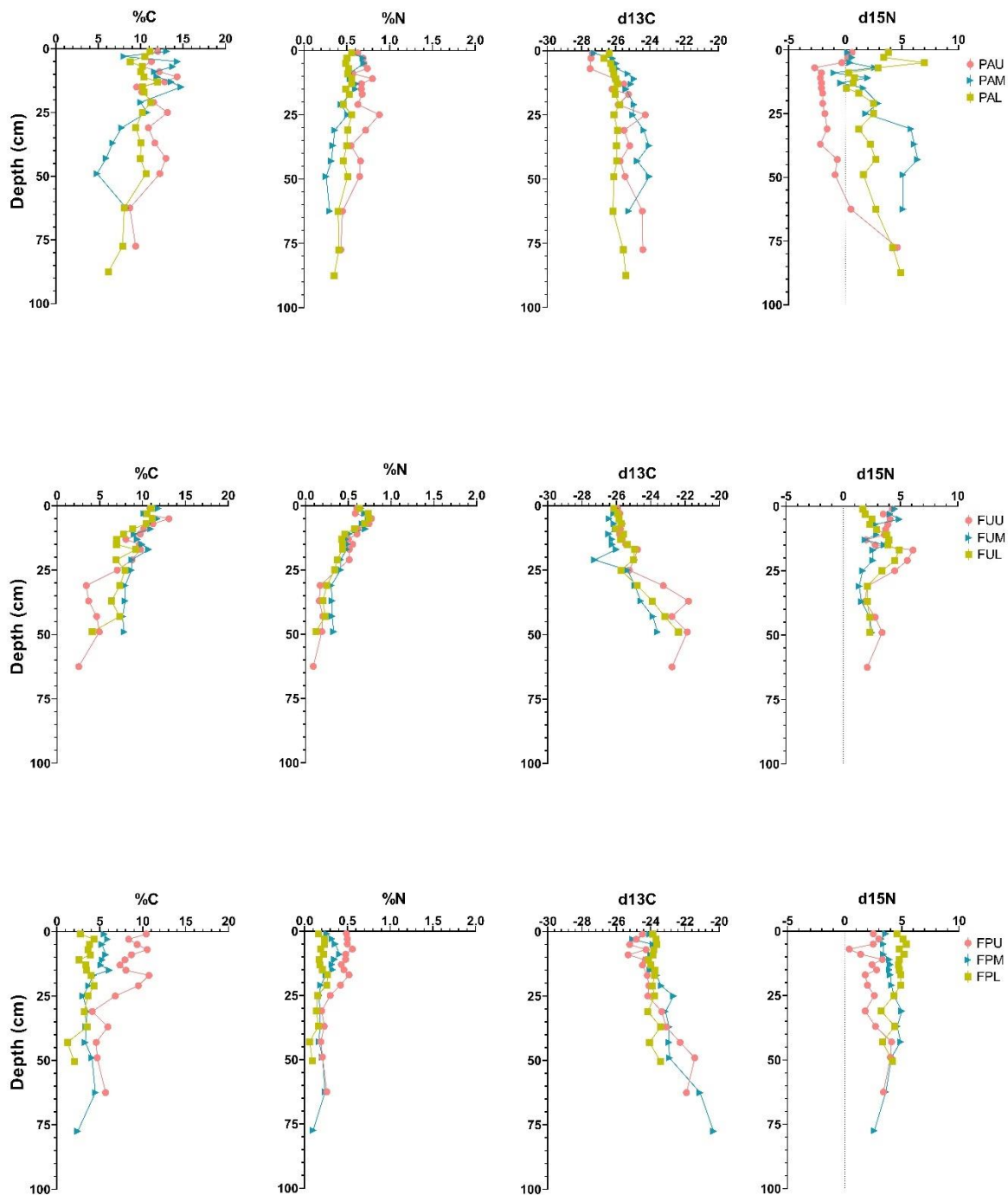


Fig. 4 – Vertical profiles of organic C (%), Total nitrogen (%), $\delta^{13}\text{C}$ (‰) and $\delta^{15}\text{N}$ (‰) in soils collected at the upper (U), middle (M), and lower (L) regions of Parati (PA), Florianópolis Urban (FU) and Florianópolis Pristine (FP) mangrove soils.

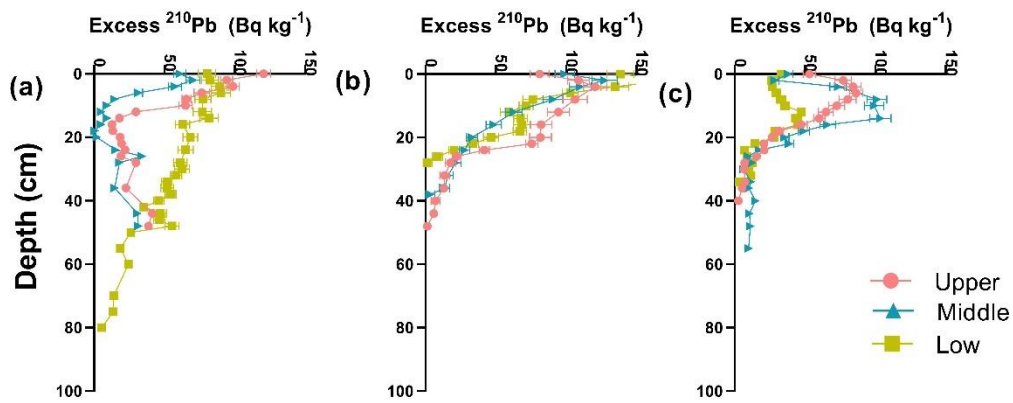


Fig. 5 – Excess ^{210}Pb specific activity profiles for mangrove soils from (a) Parati, (b) Florianópolis Urban, and (c) Florianópolis Pristine.

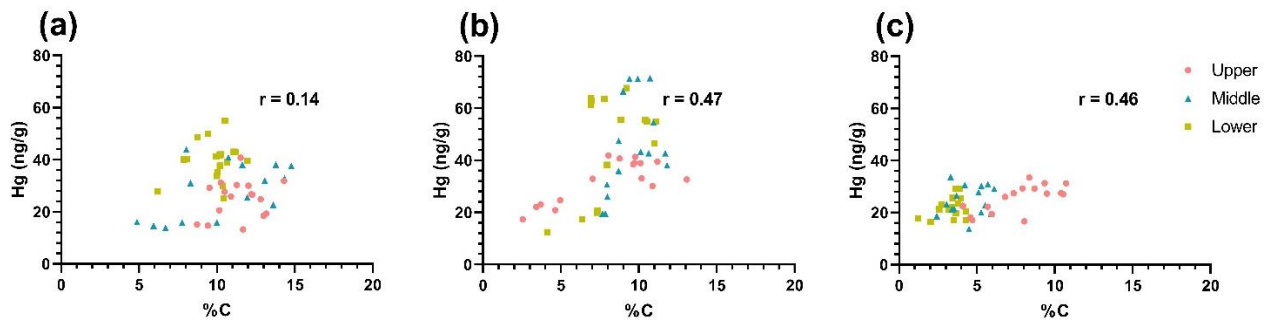


Fig. 6 – Correlation between $\%C_{\text{org}}$ and $\text{Hg}(\text{ng/g})$ and r values for each mangrove soils from (a) Parati, (b) Florianópolis Urban, and (c) Florianópolis Pristine.

SUPPLEMENTARY MATERIAL

Table S1. Sampling location and water distance. For visualization of core locations, see Fig 1.

Region	Core	Location	Distance From Water (m)
	Lower	23°18'07.1"S 44°38'57.4"W	3.0
Paraty	Middle	23°18'07.3"S 44°38'56.8"W	25.0
	Upper	23°18'07.5"S 44°38'56.1"W	50.0
	Lower	27°39'04.4"S 48°39'42.4"W	40.0
Florianópolis	Middle	27°39'03.8"S 48°39'42.1"W	60.0
Urban	Upper	27°39'03.2"S 48°39'41.8"W	80.0
	Lower	27°39'40.9"S 48°33'37.3"W	50.0
Florianópolis	Middle	27°39'41.1"S 48°33'35.8"W	80.0
Pristine		27°39'41.3"S 48°33'34.5"W	
	Upper		110.0

Table S2. Soil characteristics (mean \pm sd) for each treatment considering all plots (n = 9).

Treatment	Depth (m)	DBD (g cm ⁻³)	Silt + clay (%)	Corg (%)	N (%)	C/N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	Carbonates (%)	Hg (ng/g)
Paraty Upper	0.85	0.22 \pm 0.05	87 \pm 6	11.4 \pm 1.51	0.65 \pm 0.11	20.7 \pm 3.09	-25.8 \pm 1.05	-0.99 \pm 1.78	8.32 \pm 2.90	24.8 \pm 7.05
Paraty Middle	0.67	0.37 \pm 0.11	92 \pm 6	10.4 \pm 3.26	0.48 \pm 0.15	23.9 \pm 5.43	-25.2 \pm 0.85	2.60 \pm 2.51	6.97 \pm 3.23	25.4 \pm 10.9
Paraty Lower	0.87	0.21 \pm 0.06	96 \pm 2	9.84 \pm 1.37	0.49 \pm 0.06	23.3 \pm 1.93	-26.0 \pm 0.28	2.48 \pm 1.78	5.46 \pm 1.62	39.3 \pm 7.30
(mean \pm sd)		0.26 \pm 0.11	91 \pm 6	10.5 \pm 2.21	0.55 \pm 0.13	22.6 \pm 3.84	-25.7 \pm 0.83	1.34 \pm 2.60	6.89 \pm 2.84	30.1 \pm 10.7
Florianópolis Urban Upper	0.92	0.74 \pm 0.42	92 \pm 9	7.98 \pm 3.20	0.45 \pm 0.22	22.7 \pm 4.56	-24.7 \pm 1.47	3.52 \pm 1.24	3.14 \pm 1.30	28.6 \pm 9.40
Florianópolis Urban Middle	0.57	0.45 \pm 0.17	93 \pm 2	9.54 \pm 1.41	0.50 \pm 0.15	23.7 \pm 4.46	-25.7 \pm 1.02	2.81 \pm 1.06	4.98 \pm 1.34	40.8 \pm 19.1
Florianópolis Urban Lower	0.51	0.51 \pm 0.21	93 \pm 6	8.19 \pm 1.98	0.44 \pm 0.20	24.8 \pm 8.35	-26.1 \pm 1.12	2.97 \pm 1.02	2.95 \pm 1.63	41.1 \pm 21.7
(mean \pm sd)		0.58 \pm 0.32	93 \pm 7	8.55 \pm 2.39	0.46 \pm 0.19	23.7 \pm 5.97	-25.1 \pm 1.29	3.11 \pm 1.13	3.72 \pm 1.65	35.8 \pm 17.5
Florianópolis Pristine Upper	0.67	0.50 \pm 0.17	88 \pm 19	7.67 \pm 2.19	0.39 \pm 0.13	23.6 \pm 3.26	-23.8 \pm 1.88	2.54 \pm 0.94	3.30 \pm 1.28	24.0 \pm 5.63
Florianópolis Pristine Middle	0.97	0.72 \pm 0.19	90 \pm 26	4.45 \pm 1.14	0.25 \pm 0.09	21.3 \pm 2.91	-23.3 \pm 1.18	3.92 \pm 0.62	3.52 \pm 1.65	23.6 \pm 6.65
Florianópolis Pristine Lower	0.60	0.95 \pm 0.23	25 \pm 14	3.31 \pm 0.85	0.18 \pm 0.06	21.9 \pm 3.48	-23.8 \pm 0.22	4.57 \pm 0.64	3.81 \pm 0.82	20.8 \pm 3.71
(mean \pm sd)		0.72 \pm 0.26	70 \pm 36	5.17 \pm 2.41	0.27 \pm 0.13	22.3 \pm 3.31	-23.62 \pm 0.99	3.67 \pm 1.13	3.53 \pm 1.31	22.9 \pm 5.66

Table S3. Significant p values for Tukey or Dunn's tests performed among treatments. Significance was tested at the 0.05 level.

	Paraty vs Florianópolis Urban	Paraty vs Florianópolis Pristine	Florianópolis Urban vs Florianópolis Pristine
DBD	<0.0001	<0.0001	<0.0042
Fines			
Carbon	0.0012	<0.0001	<0.0001
Nitrogen		<0.0001	<0.0001
Carbonate	<0.0001	<0.0001	
C: N			
$\delta^{13}\text{C}$		<0.0001	<0.0001
$\delta^{15}\text{N}$	0.0028	<0.0001	
Hg		0.0021	0.0001