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IMPACTOS DE DIFERENTES DISTÚRBIOS NA ESTABILIDADE DA MATÉRIA ORGÂNICA E $\delta^{13}C$ EM SOLOS DE MANGUEZAIS

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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 a revista Limnology and Oceanography.

Orientadora: Profa. Dra. Vanessa Hatje
Co-orientador: Ms. Vinícius Patire

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APRESENTAÇÃO

Este trabalho é apresentado na forma de um manuscrito que será submetido para a revista Limnology and Oceanography.

IMPACTS OF DIFFERENT DISTURBANCES ON THE STABILITY OF ORGANIC MATTER AND $\delta^{13}C$ IN MANGROVE SOILS

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Abstract: The organic carbon (C_{org}) stocks in soils of Blue Carbon Ecosystems are composed of a mixture of macromolecules that present variable resistance to remineralization. Therefore, the disruption of mangrove soils may also result in variable carbon dioxide emissions (CO_2) due to differences in C_{org} vulnerability and environmental conditions. Here, we evaluated the degree of degradability of organic matter (OM). We used of loss on ignition (LOI) and thermogravimetric analysis (TGA) in cores of mangrove soils under different environmental pressures to understand the vulnerability of OM to degrade and its fate after remineralization. The results indicate that labile OM presented higher concentrations in the control mangroves and the lowest amounts in the shrimp ponds. Conversion of mangrove forests to shrimp ponds changes the source of OM from mangrove to phytoplankton and shrimp tissues ($\delta^{13}C_{org}$ average of -22.6 ± 2.69‰ and C:N ratio average of 8.34 ± 5.75), its degradability (94% of C_{org} is lost) and the sedimentary composition (mostly sandy) in relation to control mangroves. Mangroves receiving shrimp farm and sewage effluents are enriched with OM and N that through a 'Priming Effect' favor the remineralization of OM causing losses of 57 and 36% of C_{org}, respectively. The composition and environmental characteristics of the mangrove soils affect their ability to store C_{org} and potentially emit CO_2 under disruption, depending on their resistance to physical, chemical and microbial decomposition. Understanding the vulnerability of C_{org} in soils can help prioritizing areas for conservation, restoration, and management of Blue Carbon ecosystems.

Keywords: blue carbon, mangroves, stability, CO_2 emission, organic matter remineralization

INTRODUCTION

Mangrove forests are highly productive and one of the most carbon-rich ecosystems in the world due to its high capacity to sequester and store organic carbon (C_{org}) (Donato et al. 2011; Alongi 2014). Together with seagrasses and saltmarshes, mangroves constitute one of the Blue Carbon ecosystems (Nellemann et al. 2009). These ecosystems perform many ecological services, including an important role in nutrient and organic matter cycling (Alongi 2012). They are net autotrophic, and global rates of mangrove net primary production are high (~214 Tg C yr^{-1}; Bouillon et al. 2008; Alongi and Mukhopadhyay 2015, respectively), resulting in large C_{org} stocks in soils (~2.6 Pg C, equivalent to ~9.5 Pg of CO_2 globally) (Atwood et al. 2017).

The organic matter (OM) stored in mangrove soils comes from the autochthonous primary productivity and from allochthonous inputs from adjacent marine and/or fluvial systems (Bouillon et al. 2004; Kristensen et al. 2008). The rates of C_{org} input exceeds the decomposition rates (Ouyang et al. 2017), which makes the mangroves important carbon dioxide (CO_2) sinks (Alongi 2012; Wylie et al. 2016), mitigating the effects of climate change by sequestering greenhouse gases (Kauffman et al. 2014; Paustian et al. 2016; Ahmed et al. 2017; Rosentreter et al. 2018). However, if C_{org} soil deposits are remobilized or eroded, mangroves can act as a source of CO_2 to the atmosphere (Davidson and Janssens 2006; Sidik and Lovelock 2013; Lovelock et al. 2017b; Friesen et al. 2018).

The effects of disturbance on mangrove production and C storage have become a topic of great interest because of the mitigation strategies related to climate change. According to Macreadie (2019) one of the main issues that needs attention is the definition of the soil depth and the proportion of the disturbed C that is lost as CO_2. Both, natural and anthropogenic processes can cause long-term effects on C_{org} stocks in mangrove soils. For instance, soil temperatures can exceed 500°C during high-intensity fires, resulting in the

loss of organic matter and organic carbon, through volatilization and erosion (Pellegrini et al. 2018; Bowd et al. 2019). Logging and construction of shrimp ponds are also known to impact C_{org} contents and stocks in soils (Ahmed et al. 2017, 2018; Lovelock et al. 2017b; Kauffman et al. 2018). While the effects of human disturbances on C stocks have been largely addressed recently (Hamilton and Lovette 2015; Kauffman et al. 2016; Sasmito et al. 2016; Lovelock et al. 2017b; Friess 2019), little is known about the likelihood of carbon stocks in damaged mangrove soils to be mineralized and about other processes that could alter the fate of remineralized C_{org} in Blue C ecosystems (Howard et al. 2017; Lovelock et al. 2017a; Macreadie et al. 2017). It has been suggested that respiration, including microbial decomposition of organic matter in soils, is more sensitive to global warming that gross primary production (Woodwell 1983, Sayer et al. 2011; Cavicchioli et al. 2019). Other variables that covary with temperature, such as mineralogy, clay content, and soil water content may also constrain the decomposition rate (Davidson and Janssens 2006). Decomposition of OM in mangroves is mainly promoted by microorganisms. Bacteria and fungi respond for ~90% of the decomposition (Holguin et al. 2001) through nitrogen fixation, sulfate reduction, methanogenesis and enzyme production (Sahoo and Dhal 2009). The different types of organic compounds available on the substrate are highly associated on these degradation pathways.

The organic pool is a mixture of simple compounds that have a myriad of residence times, owing to physical or chemical protection from decomposition, and more complex compounds that have inherently low reactivity and require high activation energy for decomposition (Davidson and Janssens 2006; Burdige 2007; Kristensen et al. 2008; Arndt et al. 2013; Keuskamp et al. 2015a). For example, soils with large litter content from roots or biochar tend to contain high concentrations of recalcitrant and refractory compounds, respectively, both with high degradation resistance (Silver and Miya 2001; Capel et al.

2006), while the litterfall of leaves, flowers and fruits promotes an increase in C-rich compounds that are much more susceptible to microbial degradation (Keuskamp et al. 2015b; Friesen et al. 2018).

Due to the various controversies regarding the definitions of recalcitrant and refractory OM, it is important to establish differences about them. Recalcitrance can be defined as a set of characteristics at the level of organic substances, such as composition and molecular conformation, besides the presence of functional groups, which influence their degradation by microbes and enzymes (Kleber ,2010). Cellulose and lignin are examples of recalcitrant organic compounds (Trevathan-Tackett et al. 2017). Refractory compounds can be defined as non-metallic materials having chemical and physical properties that made them applicable for structures, or as components of systems, that can be exposed to environments above 538°C (ASTM 2009). Char is an example of a refractory composition (Capel et al. 2006). Due to controversies regarding the use of the term recalcitrance, we will employ stable or unstable organic matter to refer to the vulnerability of the organic matter degradation, which is also dependent on the environmental conditions (Kleber 2010; Schmidt et al. 2011).

The degree of inherent stability of organic matter in mangroves varies depending on species and tissue component (Wang et al. 2013; Huang et al. 2018), and allochthonous sources to C_{org} stocks, that could influence the susceptibility of remineralization of C stocks. Allochthonous refractory C stocks can bias C sequestration in Blue Carbon ecosystems since it represents only lateral transfer without new C storage and cannot be associated with net atmospheric CO_2 drawdown (Dickens et al. 2004; Leorri et al. 2018). In addition to the properties of molecules contributing to resistance to microbial degradation, the environment also influences the propensity for degradation of organic compounds, such as soil adsorption properties and the ability to promote physical

protection of molecules (Oades 1988; Spaccini et al. 2002), environmental temperature (Kirschbaum 2000) and water availability in soils (Oades 1988; McHale et al. 2005; Davidson and Janssens 2006).

We hypothesized that anthropogenic impacts such as the inputs of domestic sewage, shrimp farm effluents and the construction of shrimp farm ponds may alter the fluxes of unstable and stable C_{org} and hence the stocks of C_{org} in mangrove soils. We believe that anthropogenic activities would decrease the amount of unstable (labile) C_{org}, because the increase of allochthonous nutrients would stimulate microbial degradation. Here we studied the contents of C, $\delta^{13}C$, and also performed loss on ignition (LOI), thermogravimetry analysis (TGA) and differential thermal (DTA) in 4 sites under different degrees of anthropogenic impacts and showed how each environment condition affects C_{org} degradability in mangrove soils and hence potential to emit CO_2.

METHODS

Soil cores were collected under 4 environmental conditions (i.e., treatments), being one control and 3 impacted mangroves. For each treatment, 2 replicate cores were collected. The control treatment (MC1 and MC2) is located at the Jaguaripe estuary (Fig. S1), one of the main tributaries of the Todos os Santos Bay (12°50'S and 38°38'W), where anthropogenic activities are limited to a small shrimp farm, handmade pottery and small scale family farming (Hatje and Barros 2012). Costa et al. (2015) claim that this estuary has the best developed mangrove structure compared to other estuarine systems at the Todos os Santos Bay due to its well-preserved environmental conditions (Hatje and Barros 2012; Krull et al. 2014). The second treatment is a mangrove area under the influence of domestic sewage and solid residues inputs (IDS1 and IDS2 – Impacted mangrove that receive Domestic Sewage effluents). The third treatment is a mangrove

area that receives the effluents of a shrimp farm (ISFE1 and ISFE2 – Impacted mangrove that receives Shrimp farming Effluents). The fourth treatment is a former mangrove area converted to a shrimp pond (ISP1 and ISP2- Impacted Shrimp Pond), which has been in operation for around 30 years (Ribeiro et al. 2016). The sampling for the shrimp farm ponds was performed within the pond immediately after the harvesting.

Soil cores were collected using a stainless-steel open-faced auger. In each core, soil samples were collected up to 5 depth intervals (0-15 at 7.5 cm; 15-30 at 22 cm, 30-50 at 40 cm, 50-100 at 75 cm, and 100-200 at 150 cm), depending on soil depth, following Howard et al. (2014). Details of the collected cores are shown in Table S1.

Soil grain size was measured with a laser particle diffractometer (Cilas model 1064, France) following treatment with HCl and H_2O_2. C_{org}, total nitrogen (N) and $\delta^{13}C_{org}$ and $\delta^{15}N$ analyses were performed in the bulk fraction of the soils. Samples were acidified with 1 M HCl to remove inorganic carbon and to determine the carbonate content. C_{org}, N, $\delta^{13}C_{org}$ and $\delta^{15}N$ were determined using an elemental analyzer coupled with a Delta V Isotope Ratio Mass Spectrometer (Thermo Fisher, USA). Half of the samples were analyzed in duplicate and values of reproducibility of the method was better than ± 0.5‰ for $\delta^{13}C$ and $\delta^{15}N$. Average C_{org} recoveries for certificate reference materials (CRMs) were 99 ± 2.0%, and 102 ± 1.6%, respectively for USGS-40 and USGS-41, whereas N recoveries were 99 ± 2.6 % and 99 ± 2.3 %, respectively for USGS-40 and USGS-41.

For loss on ignition (LOI) determinations, approximately ~ 1.5 g of dry and ground sample were weighed in crucibles. Samples were oxidized over different temperatures (180°C, 300°C, 400°C, 500°C and 550°C) for 4 hours. LOI was calculated for each oxidation using the formula:

$$\text{LOI} = \frac{(\text{Pre oxidation mass} - \text{Post oxidation mass})}{\text{Pre oxidation mass}} \text{ x } 100\%$$

Interlamellar water was determined according to the mass loss at 180°C, unstable (labile) organic matter (UnOM) was characterized by mass loss at 300°C, such as hemicellulose, and stable organic matter (StOM) was characterized with the mass loss at 400°C, 500°C and 550°C, with the first temperature being the least stable OM, such as cellulose, and the last two being the most stable OM, such as lignin. To quantify soil OM (SOM), we performed a one-step oxidation at 550°C for 4 hours.

Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) were performed in a Shimadzu TG-50/DTA-50 under synthetic air flow of 50 mL, using a temperature program which consisted of four ramps with heating rate at $10^{o}C\ min^{-1}$ in the following temperature ranges: i) room temperature to $180^{o}C$ (hold at $180^{o}C$ for 5 min), ii) 180 – $300^{o}C$ (hold at $300^{o}C$ for 20 min), iii) 300 – $400^{o}C$ (hold at $400^{o}C$ for 20 min) and iv) 400 – $800^{o}C$.

To assess the differences between the environmental conditions evaluated, the one-way ANOVA statistical test ($p < 0.05$, 95 % confidence interval) was used. If ANOVA identified significant difference between groups, the Tukey HSD test ($p < 0.05$) was applied to identify which groups differed significantly from each other.

RESULTS

From LOI determinations, the SOM contents through the soil profile ranged from 1.80 ± 0.90 % (at 22 cm on ISP treatment) to 27.2 ± 4.19 % (at 22 cm on MC treatment) (Fig. 1). The control mangrove showed the highest SOM content among the evaluated conditions, with a peak of 27.2 ± 4.19 % at 22 cm followed by a reduction of contents to the base of the profile, where it reached 10.9 ± 10.5 % (Fig. 1A). The lowest concentrations were observed in the ISP, where the SOM contents ranged from 1.8 ± 0.9 % to 5.93 ± 3.98 % (Fig. 1D). With the exception of ISP, there was a tendency to reduce SOM with depth.

The degree of OM degradability, assessed by OM losses (LOI) at different temperatures, varied according to the treatment (Fig. 1, Table S2). The control mangrove had the highest of unstable OM (OM fraction lost at 300°C) value (with an average of 46.4 ± 4.15 %) (Fig. 1A, Table S2A), while the lowest value was observed for ISP (average 29.5 ± 6.11 %) (Fig. 1D, Table S2D). A decreasing trend in unstable OM was observed among the control, the IDS and cores under the influence of the shrimp farming.

C_{org} contents varied between 0.26 ± 0.01 % and 11.1 ± 2.52 % for the shrimp pond treatment and control, respectively. C_{org} showed a decrease trend, albeit with some variability, along the depth for all conditions except ISP (Fig. 2, Table S3). In general N concentrations were lower in the deepest layers and higher in the surface (Fig. 2, Table S3). The C:N ratio varied between 3.21 ± 1.39 e 29.9 ± 6.93 for the ISP e MC treatments, respectively (Fig. 2, Table S3). The profiles of C:N ratio didn't show strong vertical variation, except the cores form shrimp pond. For this treatment, the C:N ratio increased from 3.21 ± 1.39 at 7 cm to 16.1 ± 10.9 at 40 cm, where sediments presented a texture similar to the mangrove treatments (Table S3D). $\delta^{13}C_{org}$ for all mangrove treatments were similar (averages ranged from -26.8 ± 0.36 ‰ to -25.7 ± 0.50 ‰ Fig. 2, Table S3). The shrimp pond $\delta^{13}C_{org}$ was substantially smaller at the surface and decreased towards the bottom. On the other hand, $\delta^{15}N$ ranged from -3.45 ± 1.58 ‰ to 7.59 ± 3.65 ‰ (Fig. 2, Table S3).

$CaCO_3$ varied from 2.36 ± 0.50 % to 10.8 ± 0.12 % (Fig. 2, Table S3). The average value of carbonate throughout the treatments tended to decrease from MC and IDS to ISP. The control treatment presented the highest average concentration (8.26 ± 2.22 %) while ISP, the lowest (3.62 ± 0.87 %).

The grain size varied substantially between treatments (Table S3). Control mangroves and mangroves that receive domestic effluents presented mostly fine sediments (75.4 ±

19.6 % for MC and 80.8 ± 20.8 % for IDS, respectively). For the mangrove that receives effluents from shrimp farm, although fine sediments still represented a large fraction (59.3 ± 10.1 %), its importance increase along the soil profiles from 47.9 % at surface to 68.4% at the bottom, whereas only sand sediments were present at the shrimp ponds (96.5 ± 1.95 %).

TGA curves showed mass loss variations ranging from 0.56 % (at 180°C at a depth of 22 cm at ISP) to 13.6 % (at 300°C at a depth of 7 cm at MC) (Table S4). The highest average mass losses of labile (i.e. unstable OM 300°C, 9.1 ± 5.4 %) and less stable (i.e. stable OM - 400°C, 7.4 ± 4.1 %) organic fractions were associated with the control. This same treatment was the only one that presented a vertical reduction of the mass loss percentages along the whole temperature ramp (Table S4A).

For all treatments evaluated here, the distribution pattern of the percentages of mass loss in the TGA (Fig. 3) resembles the LOI data (Fig. 1). However, ISP treatment did not show a clear mass loss associated with degradation of unstable OM (at 300°C) and the less stable OM (at 400°C) in all strata except 40 cm. On the other hand, except the 7 cm,all strata of this condition presented the highest exothermic peaks in DTA curves assigned to OM oxidation above 400°C (stable OM, Fig. 3), which corroborates the LOI values presented for stable OM (Fig. 1D).

As an index of stable OM contribution in the soils evaluated here, stability index ranged from 0.16 ± 0.03 to 0.39 ± 0 (Table S5). The highest stability index values were observed for ISP, which has the lowest concentrations of C_{org}, N, C:N ratio and $CaCO_3$, with an enrichment of $\delta^{13}C_{org}$ and a reduction of $\delta^{15}N$ compared to the other treatments. No variations in stability index values along the cores were observed for treatments, except for IDS which showed an increase along depth (Table S5).

ANOVA showed a significant difference among the four treatments ($p < 0.050$, Table S6). Thus, the Tukey test was performed, to verify between which treatments there were significant differences (Table S7). SOM showed significant differences between all treatments (Tukey, $p < 0.003$, Table S7) except between MC and IDS (Tukey, $p = 0.113$, Table S7), and between IDS and ISFE (Tukey, $p = 0.116$, Table S7). When evaluating the different degrees of OM degradability, the labile fraction, UnOM, was significantly different only between MC and ISP (Tukey, $p = 0.002$, Table S7). When considering the most stable fractions (mass loss between 500 and 550 °C), StOM (OM fraction lost at 500 and 550°C), was significantly higher (Tukey, $p < 0.005$, Table S7) in ISP (36.0 ± 5.65 %) than in MC and ISFE (20.2 ± 3.09 % and 20.7 ± 3.64 %, respectively).

The Tukey test for C_{org} and N in soil profiles presented that ISP differed significantly from all other treatments (Tukey, $p < 0.020$, Table S7). For C_{org}, there was also significant differences between MC and ISFE (Tukey, $p = 0.002$, Table S7). For the N, the ISFE treatment also showed significant differences among the other treatments (Tukey, $p < 0.005$, Table S7). For $\delta^{13}C_{org}$, only ISP treatment showed significant difference compared to the others (Tukey, $p < 0.030$, Table S7), while $\delta^{15}N$ presented significant differences between all conditions (Tukey, $p < 0.090$, Table S7), except between MC and ISFE. For $CaCO_3$, all conditions presented significant difference in relation to ISP (Tukey, $p < 0.040$, Table S7). Regarding the stability index, Tukey test presented that ISP showed significant difference only with MC and ISFE (Tukey, $p < 0.007$, Table S7).

DISCUSSION

We observed that different anthropogenic impacts, i.e. effluents from shrimp farms, domestic effluents and shrimp farming ponds, significantly, influenced soil profile characteristics. The most significant difference, when compared to the control site, was

observed for the SOM, C_{org}, $\delta^{13}C_{org}$, $\delta^{15}N$ measured in the ISP. We also noted that unstable OM concentrations decrease while stable OM increase under anthropogenic influence. This result indicates that anthropogenic impacts promote greater remineralization of fresh OM, especially in areas where conversion of mangrove into shrimp pond occured. Anthropogenic activities seem to impact C_{org} concentrations along the 1 m profiles for all impacted treatments and up to 2 m soil, as seen in ISFE.

The conversion of mangrove areas into shrimp farming has increased since 1980 and the consequences of this conversion have a strong impact on C dynamics in Blue Carbon ecosystems (Ahmed et al. 2017). Shrimp farming requires a constant supply of nutrients, which stimulate phytoplankton production. The phytoplankton-produced OM contributes to the SOM concentrations, performing low C:N ratio values (Fig. 2 and 4). Beside to the contribution of phytoplankton, it is likely that shrimp tissue debris also contribute to SOM contents with the highest stability index recorded among all treatments and also due to the high $\delta^{13}C_{org}$ values ($\delta^{13}C_{org}$ of -18.8 ± 1.24 ‰ at 7 cm and -22.8 ± 1.67 ‰ at 22 cm, Fig. 2, Table S3D), characteristic of the *Litopenaeus vannamei* cultivated in the region ($\delta^{13}C_{org}$ ranging from -23.4 ‰ to -14.9 ‰; Li et al. 2018).

The construction of shrimp ponds, after deforestation of mangroves, changes the sedimentary texture of soils from the muddy to sandy (Barbier et al. 2011). Geochemically, clay is characterized by the ability to adsorb organic compounds at active sites on their particle surface (Oades 1988), which does not occur with sandy sediments. Thus, ISP SOM is more prone to be transported/exported during harvesting cycles. At this stage of the shrimp cultivation process, the entire volume of water from the tank is drained to the adjacent mangrove areas, carrying large amounts of nutrients and fresh OM not retained in the tank soil (Ribeiro et al. 2016).

After the harvesting, the soil is left to dry and it is them manualy remobilized exposing deeper portions of the reducing soil profile to the oxidizing atmosphere and high temperatures. Both factors promote an increase in microorganism development rates, associated with low C:N ratios (Fig. 2, Table S3D) and low $\delta^{15}N$ values (-3.45 ± 1.58 ‰ at 22 cm and -2.79 ± 0.69 ‰ at 75 cm in ISP, Fig. 2, Table S3D) (Silver and Miya 2001; Trumbore and Czimczik 2008; Simpson and Simpson 2012), followed by remineralization of SOM in CO_2 and thus becoming a source of this greenhouse gas to the atmosphere.

Associated with the soil destabilization, the mangrove conversion on shrimp ponds results in lower $CaCO_3$ contents and SOM and unstable OM compared to all other treatments both by LOI and by TGA mass loss. Also a change in the source of OM, especially in the layers above 40 cm, which present an enrichment of $\delta^{13}C_{org}$, is related to particulate organic matter that is brought by water stored in the tank for shrimp cultivation and the tissues of the shrimps themselves (Fig. 4, adapted from Lamb et al. 2006). However, below the 40 cm layer the OM and soil texture shows characteristics similar to those of the pre-existing mangrove ecosystem before conversion.

All the water from the pond during harvesting flows into the adjacent mangrove. This effluent is rich in nutrients and fresh OM (Prasad 2012; Suárez-Abelenda et al. 2014). This energy-rich supply of fresh OM is a stimulant for microbial development called priming effect (Löhnis 1926; Fontaine et al. 2003, 2007; Guenet et al. 2010). This effect represents a stimulus for nutrient-limited organisms specialized in fresh OM decomposition, called r - strategists. (Jenkinson 1971; Fontaine et al. 2003; Guenet et al. 2010), resulting in the reduction in the concentrations of unstable OM illustrated by both LOI and by TGA data. The increase in microbial decomposition with the contribution of energetically rich compounds from the shrimp pond tends to produce compounds rich in ^{15}N, increasing the $\delta^{15}N$ (1.89 ± 0.65 ‰ Fig. 2, Table S3C) compared to ISP (-2.07 ± 1.28 ‰, Fig. 2, Table

S3D), besides the reduction in C_{org} concentrations due to microbial degradation, resulting in low C:N ratios (15.4 ± 1.85, Fig. 2, Table S3C) compared to MC (25.9 ± 2.65, Fig. 2, Table S3A).

In both treatments impacted by shrimp farming (ISP and ISFE) there is a reduction in C_{org} concentrations compared to MC, a standard that is also documented for many mangrove soils around the world, such as Malaysia (Eong 1993), Australia (Lovelock et al. 2017a), Dominican Republic (Kauffman et al. 2014) and Saudi Arabia (Eid et al. 2019). On the other hand, the SOM presented a relatively constant vertical distribution, but with smaller values in relation to the control mangrove, which is a common pattern in mangrove soils receiving shrimp farming effluents (Ahmed et al. 2017).

The domestic effluents, that impact the IDS cores, present high concentrations of N that also stimulate the microbial activity of fresh OM decomposers, also suggesting the occurrence of priming effects (Jenkinson 1971; Kuzyakov et al. 2000; Fontaine et al. 2003, 2007; Guenet et al. 2010). This contribution induces the increase of discriminatory processes by the microbial fauna, such as OM remineralization, which synthesize compounds with high concentrations of ^{15}N (Lovelock et al. 2009; Zhou et al. 2014), promoting the highest values of $\delta^{15}N$ in this treatment (5.81 ± 1.19 ‰, Fig. 2, Table S3B). The stimulation of this positive priming effect reduces unstable OM, shown by LOI and TGA and also reducing C_{org} (5.86 ± 1.64 %), compared to the control.

In terms of comparison between the two treatments in which priming effect occurs (ISFE and IDS) the C:N ratio values decrease in ISFE, indicating that sewage input favors optimal microbial development (Silver and Miya 2001). Even though they are subjected to the same priming process, sporadic harvesting events tend to make the ISFE environment more limiting to fresh N and OM, and have almost half of their sedimentary texture

characterized as sand (Table S3C). Thus, ISFE has a higher impact when compared to IDS, whose limiting aspect of fresh N and OM is smaller.

Some studies considering C_{org} losses in impacted mangroves consider only 1 m of soil in their assessments (Pendleton et al. 2012). However, losses below 1 m of soil depth are also important (Kauffman et al. 2018), which have been documented in Malaysia and Dominican Republic when considering mangrove conversion to shrimp ponds (Eong 1993; Kauffman et al. 2014). Considering 1 m of soil, C_{org} losses represent 93.5 %, 56.6 % and 36.3 % for ISP, ISFE and IDS, respectively, when compared to MC. For ISFE, considering only the interval between 1 and 2 m of soil, C_{org} losses represent a total of 31.8 % in relation to the same depth in the control area. The mangrove conversion thus contributes as a source of large amounts of CO_2 to the atmosphere as a result of stimulating microbial activity and, consequently, increased degradation of OM in ISP, ISFE and IDS.

Given the responses of anthropogenic impacts on the ecosystems evaluated here, it is important to highlight the need to determine the level of anthropogenic impact in areas used to estimate C stocks in Blue Carbon ecosystems. This is justified, for example, by estimating C_{org} stocks in an ISFE-like area and extrapolating to a region, which will tend to induce an error of approximately 56.6 % in C_{org} stocks in this region, underestimating such stocks. On the other hand, estimates using control areas may overestimate C stocks. Therefore, to consider the carbon footprint of the landscape of each ecosystem, defined as the greenhouse gases that are released from the conversion of natural ecosystems (Kauffman et al. 2017), is fundamental to estimate with greater precision the C stocks.

CONCLUSION

We observed that different types of anthropogenic impacts may change the degree of OM degradability and C_{org} concentration in mangrove soils. Unstable organic matter is more abundant in well preserved systems. In the occurrence of priming effects in impacted areas, we observed an increase in the amount of stable organic matter possible resulting from the loss of organic matter through CO_2 emission into the atmosphere.

Our findings provide a contribution to the understanding of SOM biogeochemistry under anthropogenic impacts in mangroves, which is a current hot topic under climate change mitigation discussions. Given this, the strategies adopted for the conservation and management of Blue Carbon ecosystems may consider which anthropogenic activities may influence C_{org}'s biogeochemistry in each ecosystem.

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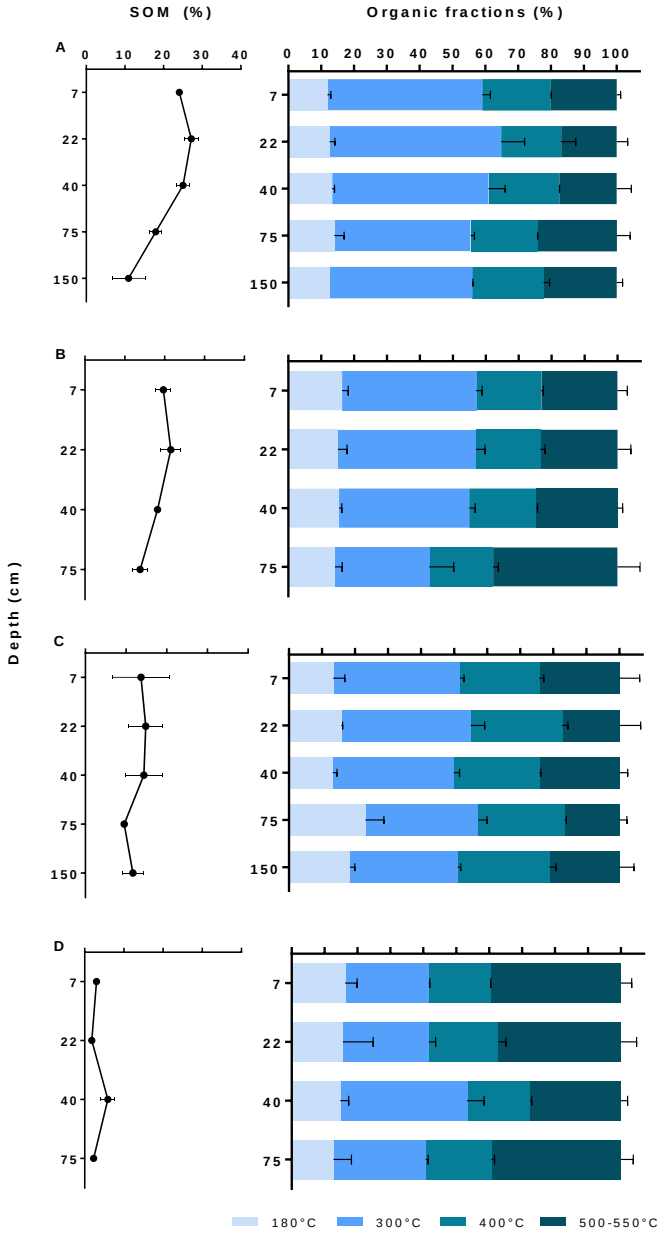

Figure 1. Contents of SOM (%, dry weight) and percentage of organic matter lost along the oxidation processes for Control Mangrove (MC; A), Impacted mangrove that receive Domestic Sewage (IDS; B), Impacted mangrove that receive Shrimp Farming Effluents (ISFE; C) and Impacted Shrimp Pond (ISP; D). Values are mean ± standard error. There are only data for the depth of 150 cm for the MC and ISFE treatments because they were the only ones sampled to this depth.

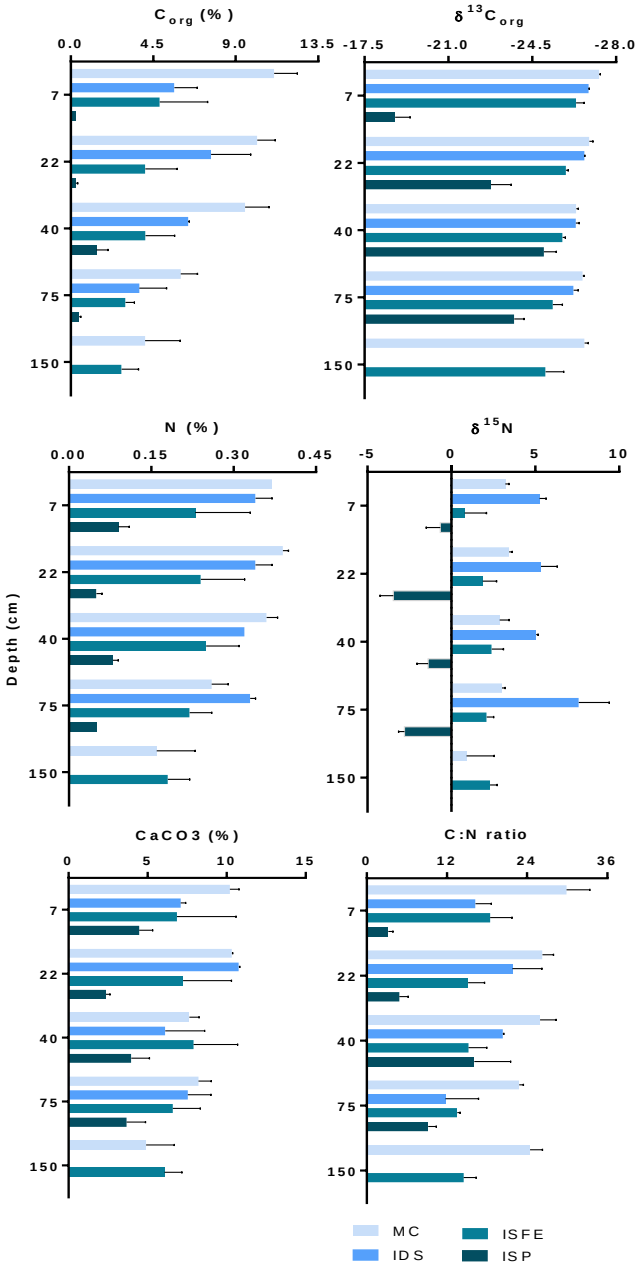

Figure 2. Mean and standard error for C_{org}, N, $\delta^{13}C_{org}$, $\delta^{15}N$, C/N ratio and carbonates for fixed depths of soil profiles of control and impacted mangrove areas (Impacted mangrove that receive Domestic Sewage, IDS; Impacted mangrove that receive Shrimp Farming Effluents, ISFE; Impacted Shrimp Pond, ISP). There are only data for the depth of 150 cm for the MC and ISFE treatments because they were the only ones sampled to this depth.

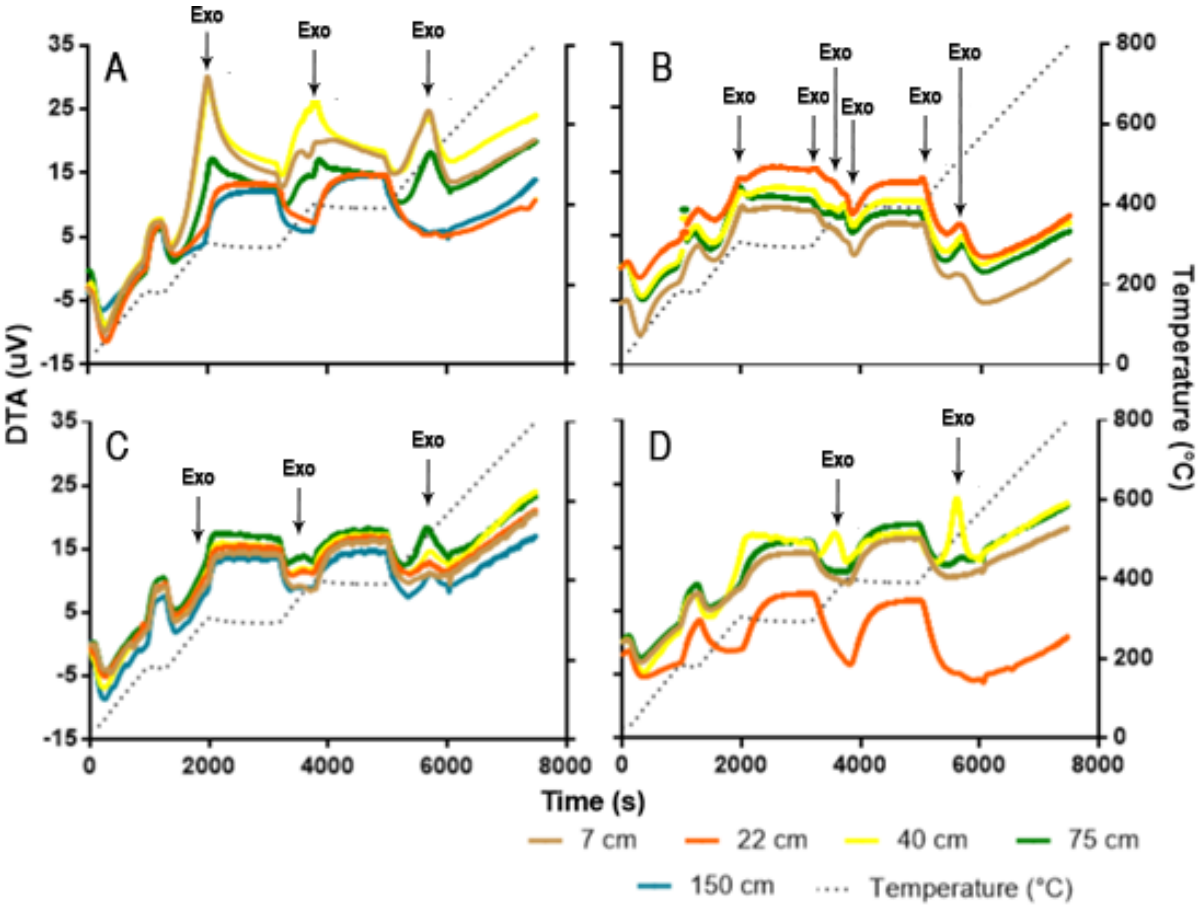

Figure 3. DTA curves for Control Mangrove (MC; A), Impacted mangrove that receive Domestic Sewage (IDS; B), Impacted mangrove that receive Shrimp Farming Effluents (ISFE; C) and Impacted Shrimp Pond (ISP; D). There are only data for the depth of 150 cm for the MC and ISFE treatments because they were the only ones sampled to this depth.

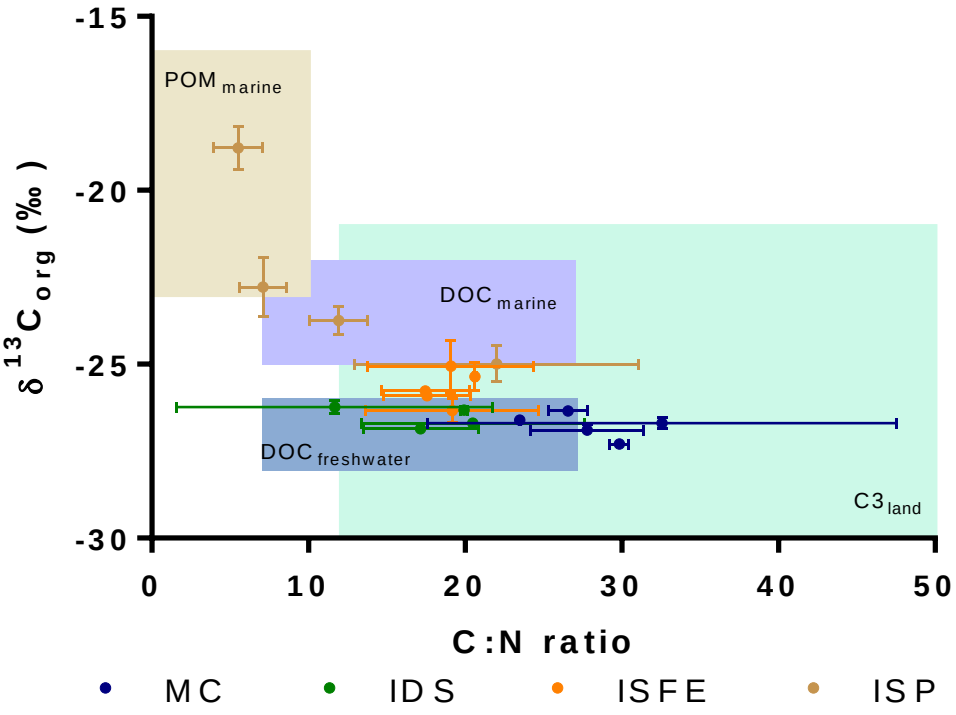

Figure 4. Relationship between C:N ratio and $\delta^{13}C_{org}$ to identify the sources of OM in the four treatments (Control Mangrove, MC; Impacted mangrove that receive Domestic Sewage; IDS; Impacted mangrove that receive Shrimp Farming Effluents; ISFE; and Impacted Shrimp Pond, ISP). Adapted from Lamb et al. (2006). Values are mean and standard error.

SUPPLEMENTARY MATERIAL

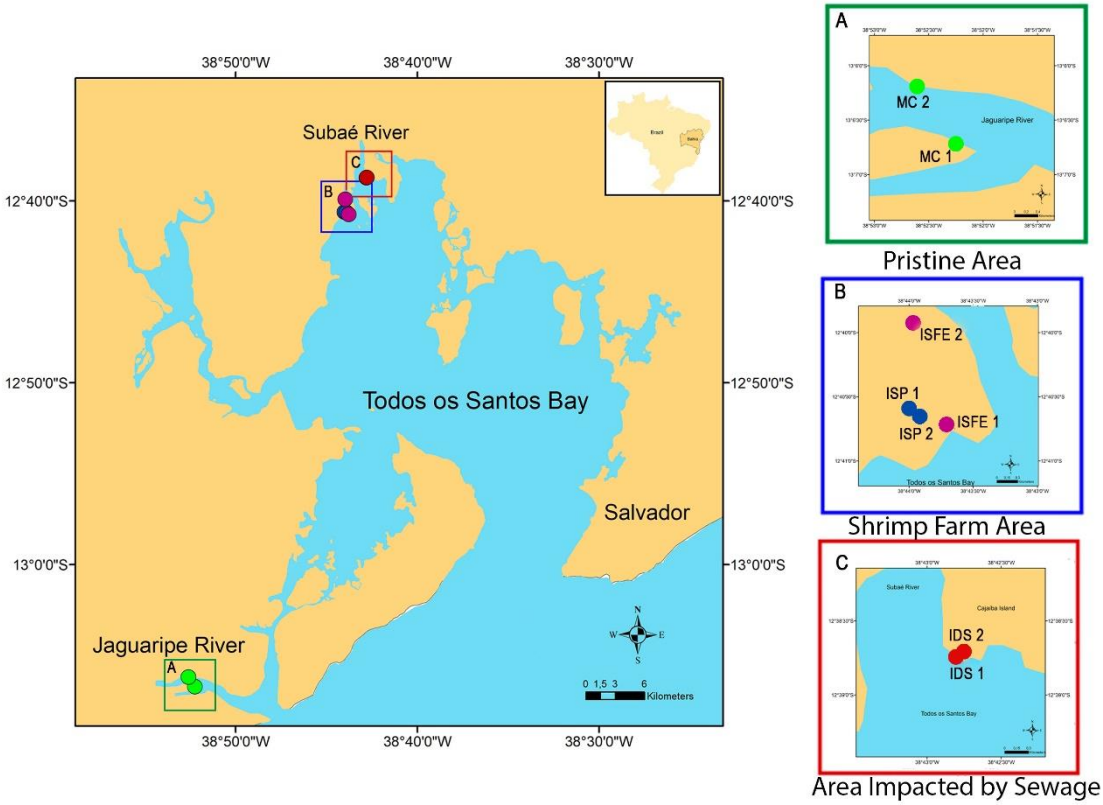

Figure S1. Study area showing the location of the collected cores in the four treatments (i.e. control area. MC1 and MC2, panel A); shrimp pond (ISP1 and ISP2) and mangroves that receive shrimp farm effluents (ISFE 1 and ISFE2, panel B); and mangrove impacted by domestic effluents and solid residues (IDS1 and IDS2, panel C).

Table S1. Location and characteristics of the core.

Treatment	Core	Location	Length of the core (cm)
Control (MC)	MC1	13°06’13.1”S 038°52’39.4”W	200
	MC2	13°06’44.3”S 038°52’14.9”W	200
Impact domestic sewage (IDS)	IDS1	12°38’43.3'”S 038°42’47.8'”W	~100
	IDS2	12°38’42.8”S 038°42’47.0”W	~100
Impact shrimp farm effluents (ISFE)	ISFE1	12°40’44.8”S 038°43’47.6'”W	200
	ISFE2	12°39’54.9”S 038°43’58.5”W	200
Impact shrimp pond (ISP)	ISP1	12°40’01,0'”S 038°43’58,2'”W	~100
	ISP2	12°40’40,3'”S 038°43’55,0'”W	~100

Table S2. Average (± standard deviation) of organic fraction percentages for each treatment

(A) Control treatment

Depth (cm)	180°C	UnOM (300°C)	StOM (400°C)	StOM (500 – 550°C)
7	11.9 (±1.96)	47.1 (±5.01)	20.8 (±0.64)	20.2 (±2.41)
22	12.6 (±2.22)	52.2 (±10.1)	18.2 (±3.16)	16.9 (±4.74)
40	13.3 (±1.03)	47.6 (±7.23)	21.5 (±0.10)	17.5 (±6.30)
75	14.0 (±5.98)	41.5 (±2.46)	20.3 (±0.22)	24.2 (±8.22)
150	12.7 (±0.03)	43.4 (±0.13)	21.6 (±3.73)	22.3 (±3.57)

(B) Mangrove impacted by domestic effluents and solid residues

Depth (cm)	180°C	UnOM (300°C)	StOM (400°C)	StOM (500 – 550°C)
7	16.4 (±3.62)	40.6 (±3.67)	19.8 (±1.26)	23.1 (±6.03)
22	15.1 (±5.59)	42.0 (±5.51)	19.4 (±3.04)	23.5 (8.06)
40	15.5 (1.58)	39.5 (±3.72)	20.3 (±0.94)	24.8 (±3.09)
75	14.2 (±4.40)	28.6 (±14.9)	19.4 (±3.22)	37.8 (±13.8)

(C) Mangrove area that receives the effluents of a shrimp farm

Depth (cm)	180°C	UnOM (300°C)	StOM (400°C)	StOM (500 – 550°C)
7	13.4 (±6.99)	38.3 (±6.99)	24.0 (±2.75)	24.2 (±12.2)
22	15.9 (±0.79)	39.2 (±8.46)	27.6 (±3.65)	17.4 (12.9)
40	13.3 (±2.45)	36.6 (±3.41)	25.9 (±0.88)	24.2 (±4.99)
75	23.2 (±11.1)	34.1 (±5.34)	26.1 (±1.18)	16.6 (±4.60)
150	18.5 (±2.97)	32.7 (±1.72)	27.7 (±4.14)	21.2 (±8.84)

(D) Mangrove area converted to a shrimp pond

Depth (cm)	180°C	UnOM (300°C)	StOM (400°C)	StOM (500 – 550°C)
7	16.2 (±7.22)	25.4 (±0.55)	18.8 (±0.14)	39.6 (±6.54)
22	15.5 (±18.4)	18.4 (±4.14)	21.0 (±4.75)	37.3 (±9.56)
40	14.8 (±5.08)	38.5 (±10.3)	19.0 (±1.14)	27.6 (±4.11)
75	12.7 (±11.0)	28.0 (±1.51)	19.9 (±1.94)	39.4 (±7.52)

Table S3. Mean (± standard deviation) for C_{org}, $\delta^{13}C_{org}$, N, $\delta^{15}N$, $CaCO_3$, C:N ratio and grain size.

(A) Control treatment

Depth (cm)	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	N (%)	$\delta^{15}N$ (‰)	$CaCO_3$ (%)	C:N ratio	Grain size (%)		
							Clay	Silt	Sand
7	11.1 (±2.52)	-27.3 (±0.11)	0.37 (±0.01)	3.22 (±0.43)	10.2 (±1.39)	29.9 (±6.93)	7.76	73.8	18.4
22	10.2 (±1.93)	-26.9 (±0.27)	0.39 (±0.02)	3.45 (±0.36)	10.3 (±0.12)	26.3 (±3.30)	5.03	75.2	19.8
40	9.51 (±2.63)	-26.3 (±0.19)	0.36 (±0.03)	2.88 (±1.13)	7.64 (±1.52)	25.9 (±4.84)	4.90	82.4	12.7
75	6.00 (±1.82)	-26.6 (±0.11)	0.26 (±0.07)	3.02 (±0.37)	8.22 (±2.00)	22.8 (±1.25)	5.46	81.4	13.1
150	4.06 (±3.82)	-26.7 (±0.29)	0.16 (±0.13)	0.91 (±3.28)	4.90 (±4.40)	24.4 (±3.70)	2.92	37.8	54.3

(B) Mangrove impacted by domestic effluents and solid residues

Depth (cm)	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	N (%)	$\delta^{15}N$ (‰)	$CaCO_3$ (%)	C:N ratio	Grain size (%)		
							Clay	Silt	Sand
7	5.65 (±2.50)	-26.9 (±0.04)	0.34 (±0.06)	5.25 (±0.78)	7.09 (±0.63)	16.3 (±4.73)	7.87	79.4	12.8
22	7.65 (±4.34)	-26.7 (±0.02)	0.34 (±0.06)	5.34 (±1.92)	10.8 (±0.12)	21.8 (±8.81)	7.22	79.6	13.2
40	6.42 (±0.09)	-26.3 (±0.28)	0.32 (±0.01)	5.06 (±0.22)	6.12 (±4.97)	20.3 (±0.32)	8.49	82.0	9.53
75	3.74 (±2.99)	-26.2 (±0.37)	0.33 (±0.02)	7.59 (±3.65)	7.55 (±2.91)	11.8 (±9.91)	9.32	86.6	4.09

(C) Mangrove area that receives the effluents of a shrimp farm

Depth (cm)	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	N (%)	$\delta^{15}N$ (‰)	$CaCO_3$ (%)	C:N ratio	Grain size (%)		
							Clay	Silt	Sand
7	4.85 (±5.23)	-26.3 (±0.67)	0.23 (±0.20)	0.79 (±2.61)	6.85 (±7.49)	18.4 (±6.55)	2.83	45.1	52.1
22	4.07 (±3.48)	-25.9 (±0.18)	0.24 (±0.15)	1.87 (±1.66)	7.24 (±6.12)	15.2 (±4.88)	6.11	45.3	48.6
40	4.08 (±3.15)	-25.8 (±0.22)	0.25 (±0.12)	2.40 (±1.39)	7.91 (±5.57)	15.2 (±5.44)	5.51	52.3	42.2
75	2.99 (±0.95)	-25.4 (±0.80)	0.22 (±0.08)	2.11 (±0.82)	6.59 (±3.49)	13.5 (±0.86)	5.17	65.7	29.2
150	2.77 (±1.83)	-25.1 (±1.50)	0.18 (±0.08)	2.31 (±0.83)	6.07 (±2.20)	14.5 (±3.72)	5.51	62.9	31.6

(D) Mangrove area converted to a shrimp pond

Depth (cm)	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	N (%)	$\delta^{15}N$ (‰)	$CaCO_3$ (%)	C:N ratio	Grain size (%)		
							Clay	Silt	Sand
7	0.26 (±0.01)	-18.8 (±1.24)	0.09 (±0.04)	-0.65 (±1.75)	4.46 (±1.70)	3.21 (±1.39)	1.84	3.95	94.2
22	0.27 (±0.23)	-22.8 (±1.67)	0.05 (±0.02)	-3.45 (±1.58)	2.36 (±0.50)	4.86 (±2.64)	0.71	1.07	98.2
40	1.40 (±1.26)	-25.0 (±1.04)	0.08 (±0.03)	-1.38 (±1.31)	3.97 (±2.29)	16.1 (±10.9)	1.40	3.04	95.6
75	0.46 (±0.16)	-23.7 (±0.83)	0.05 (±0.01)	-2.79 (±0.69)	3.67 (±2.41)	9.20 (±2.37)	1.11	1.98	98.0

Table S4. Weight loss associated to each studied temperature for DTA analysis.

(A) Control treatment

Depth (cm)	Weight loss (%)			
	180°C	300°C	400°C	400-800°C
7	6.21	13.6	10.9	3.41
22	5.60	13.3	11.3	3.88
40	6.60	11.6	8.37	4.70
75	3.29	5.54	4.67	2.92
150	0.69	1.43	1.72	0.86

(B) Mangrove impacted by domestic effluents and solid residues

Depth (cm)	Weight loss (%)			
	180°C	300°C	400°C	400-800°C
7	8.36	6.87	5.88	7.18
22	7.30	8.67	7.23	9.60
40	4.73	5.29	5.36	6.89
75	4.30	5.37	5.69	7.23

(C) Mangrove area that receives the effluents of a shrimp farm

Depth (cm)	Weight loss (%)			
	180°C	300°C	400°C	400-800°C
7	1.04	1.54	1.04	1.02
22	2.43	2.23	1.84	2.15
40	3.10	2.08	2.14	2.86
75	2.58	2.76	3.80	3.11
150	2.55	1.81	2.06	3.16

(D) Mangrove area converted to a shrimp pond

Depth (cm)	Weight loss (%)			
	180°C	300°C	400°C	400-800°C
7	1.18	1.00	0.85	2.09
22	0.56	0.81	0.61	1.18
40	1.47	2.62	2.20	400-600: 2.45 600-800: 1.07
75	0.75	0.72	0.73	0.96

Table S5. Average (± standard deviation) of stability index for each treatment (Control Mangrove, MC; Impacted mangrove that receive Domestic Sewage, IDS; Impacted mangrove that receive Shrimp Farming Effluents, ISFE; and Impacted Shrimp Pond, ISP). Only MC and ISFE treatments were sampled depths at 150 cm.

Depth (cm)	MC	IDS	ISFE	ISP
7	0.20 (±0.02)	0.23 (±0.05)	0.24 (±0.12)	0.39 (±0.05)
22	0.18 (±0.04)	0.23 (±0.07)	0.17 (±0.11)	0.37 (±0.08)
40	0.19 (±0.05)	0.25 (±0.03)	0.24 (0.04)	0.28 (±0.04)
75	0.24 (±0.07)	0.38 (±0.11)	0.16 (±0.04)	0.39 (±0.06)
150	0.22 (±0.03)		0.21 (±0.07)	

Table S6. One-way Anova test performed for each variable between treatments. For this test. the 150 cm depth was not included in the analysis as it was sampled for only two of the four treatments.

(A) SOM

	Sum of sqrs	df	Mean square	F	p
Between groups	900.4	3	300.1	33.70	< 0.001
Within groups	106.9	12	8.906		
Total	1007	15			

(B) UnOM (300°C)

	Sum of sqrs	df	Mean square	F	p
Between groups	622.4	3	207.4	8.375	< 0.001
Within groups	297.2	12	24.77		
Total	919.6	15			

(C) StOM (400°C)

	Sum of sqrs	df	Mean square	F	p
Between groups	109.2	3	36.39	27.15	< 0.001
Within groups	16.09	12	1.340		
Total	125.3	15			

(D) StOM (500 – 550°C)

	Sum of sqrs	df	Mean square	F	p
Between groups	678.5	3	226.2	8.245	< 0.001
Within groups	329.2	12	27.43		
Total	1008	15			

(E) C_{org}

	Sum of sqrs	df	Mean square	F	p
Between groups	154.9	3	51.63	24.20	< 0.001
Within groups	25.60	12	2.133		
Total	180.5	15			

(F) N

	Sum of sqrs	df	Mean square	F	p
Between groups	0.197	3	0.065	64.87	< 0.001
Within groups	0.012	12	0.0010		
Total	0.209	15			

(G) $\delta^{13}C_{org}$

	Sum of sqrs	df	Mean square	F	p
Between groups	45.42	3	15.14	7.931	0.004
Within groups	22.91	12	1.909		
Total	68.33	15			

(H) $\delta^{15}N$

	Sum of sqrs	df	Mean square	F	p
Between groups	129.2	3	43.06	47.64	< 0.001
Within groups	10.85	12	0.904		
Total	140.0	15			

(I) C:N ratio

	Sum of sqrs	df	Mean square	F	p
Between groups	649.7	3	216.6	13.13	< 0.001
Within groups	197.9	12	16.49		
Total	847.6	15			

(J) $CaCO_3$

	Sum of sqrs	df	Mean square	F	p
Between groups	66.62	3	22.21	12.55	< 0.001
Within groups	21.24	12	1.770		
Total	87.85	15			

(K) Stability index

	Sum of sqrs	df	Mean square	F	p
Between groups	0.065	3	0.022	8.2	0.003
Within groups	0.032	12	0.003		
Total	0.097	15			

Table S7. Values of P for Tukey HSD test performed for each variable between treatments when ANOVA presented $p < 0.050$. For this test, the 150 cm depth was not included in the analysis as it was collected for only two of the four treatments.

	SOM	UnOM (300°C)	StOM (400°C)	StOM (500 – 550°C)	C_{org}	N	$\delta^{13}C_{org}$	$\delta^{15}N$	C:N ratio	$CaCO_3$	Stability index
MC– IDS	0.11	0.08	0.93	0.22	0.03	0.94	0.99	<0.01	0.05	0.58	0.28
MC– ISFE	<0.01	0.06	<0.01	0.99	<0.01	<0.01	0.77	0.24	0.01	0.22	1.00
MC– ISP	<0.01	<0.01	0.92	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
IDS– ISFE	0.12	1.00	<0.01	0.32	0.32	<0.01	0.90	<0.01	0.90	0.86	0.30
IDS– ISP	<0.01	0.15	1.00	0.14	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	0.13
ISFE- ISP	<0.01	0.19	<0.01	<0.01	0.03	<0.01	0.03	<0.01	0.11	0.01	<0.01