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Greenhouse Gas Fluxes and Carbon Stock in Conserved and Degraded Mangroves

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Abstract

Mangrove degradation in tropical areas is an alarming phenomenon with significant local and global consequences for greenhouse gas (GHG) emissions and carbon storage (SCS). In this study, seasonal fluxes of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) from soil and SCS were evaluated in mangroves with different ecological conditions (conserved and degraded) in the western coastal sector of Campeche, Mexico. The highest CO_2 fluxes (1108.5 to 1563.7mg m^{-2} h^{-1}) were recorded during the dry season in the conserved mangroves. CH_4 fluxes were highest in the most degraded mangroves during the wet season (6071.4 to 6675.47μg m^{-2} h^{-1}). N_2O fluxes did not show significant differences between treatments ($p>0.05$), with the highest fluxes occurring during the rainy season in the Atasta mangrove forest (713.6 ± 258.1μg m^{-2} h^{-1}). The highest contribution to global warming potential among seasons and sites was CO_2 (62.2 ± 34.1 Mg CO_2-eq ha^{-1} yr^{-1}), followed by N_2O (15.7 ± 4.5 Mg CO_2-eq ha^{-1} yr^{-1}) and finally CH_4 with the lowest CO_2-eq contribution of 9 ± 5.7 Mg CO_2-eq ha^{-1} yr^{-1}. The conserved mangroves stored an average of 503.6 ± 96.7 Mg C ha^{-1} and the more degraded mangroves stored 275.1 ± 25 Mg C ha^{-1}. The results of the present study suggest that GHG emissions and SCS are strongly influenced by site ecological conditions, seasonality and variation in some soil properties so that the ecological degradation of mangroves can increase GHG emissions and reduce the ecosystem's capacity to store carbon.

Keywords Tropical mangroves; GHG fluxes; Soil carbon storage

Introduction

The continuous and massive release of greenhouse gases (GHG) has led to a global rise in Earth's temperature. GHGs are emitted from fossil fuel combustion and use, industrial activities, agriculture, land use change and natural sources. The natural sources such as wetlands that are among the most carbon-rich natural ecosystems in the world [1]. Coastal wetlands such as mangroves found in tropical and subtropical regions, are unique ecosystems that play a crucial role in coastal stability. They protect against extreme weather events, provide vital habitats for numerous marine and terrestrial species, and offer a variety of ecosystem services including high rates of carbon sequestration and storage [2-5].

In recent decades, mangroves have experienced a high degradation rate due to various anthropogenic factors, such as conversion for agriculture, aquaculture, urban development, pollution, and natural resource extraction [6]. The rate of degradation results in the loss of habitats and biodiversity, as well as the disruption of ecosystem services involving global climate change [7,8].

One of the most significant impacts of mangrove degradation is its contribution to GHG emissions, particularly carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Mangroves are effective carbon sinks, storing large amounts of carbon in their biomass and soil. However, when degraded or destroyed, this stored carbon is released back into the atmosphere [9,10]. In addition, mangrove degradation also leads to the decomposition of accumulated organic matter in the soil, releasing more CO_2 and CH_4 into the atmosphere.

The emission of GHG in mangroves depends on the variation of physicochemical and environmental parameters such as the sediment grain size, the extent of flooding and temperature, the intertidal position, the redox conditions of sediments, the soil pH and salinity [11].

The dynamics of GHG emission and carbon accumulation in mangrove soils in tropical regions, like Mexico, have been scarcely studied despite carbon stocks in Mexican mangroves ranging from 79 to 647 Mg ha^{-1} [12]. It has been estimated the total carbon stock in degraded mangroves of the country is 349 ± 6 Tg C and emits an annual average of 0.09 ± 0.04 Tg CO_{2e} yr^{-1} [13].

Our objective was to measure the variation in soil CO_2, CH_4 and N_2O fluxes in mangroves with different conditions of ecological degradation to determine whether degraded mangrove soil is a significant source of CO_2, CH_4 and N_2O, besides quantify the carbon stock in both well-preserved and degraded mangroves and identify the major environmental factors affecting soil GHG flux and carbon storage.

Materials and Methods

Study site description

The study area is in the south of the Gulf of Mexico, in the western sector of the coast of Campeche, in between Nuevo Campechito and Boca Nueva, on the shore of the Natural Protected Area Terminos Lagoon in Carmen Island, Campeche, Mexico (Figure 1). The diversity in species and habitats, the marine resources, the interrelation with Campeche Sound (an important fishing area in the Gulf of Mexico), make this site one of Mexico's most important lagoon systems. It is part of the National Flora and Fauna Reserve Terminos Lagoon that comprises 705,016ha of open water and associated wetlands and upland, including associated lagoons and channels, with an average depth of 4m, surrounded by 259,000ha of mangrove and marsh [14]. The region is part of the ecological complex of the coastal plain that controls the deltaic processes of the Grijalva-Usumacinta River system.

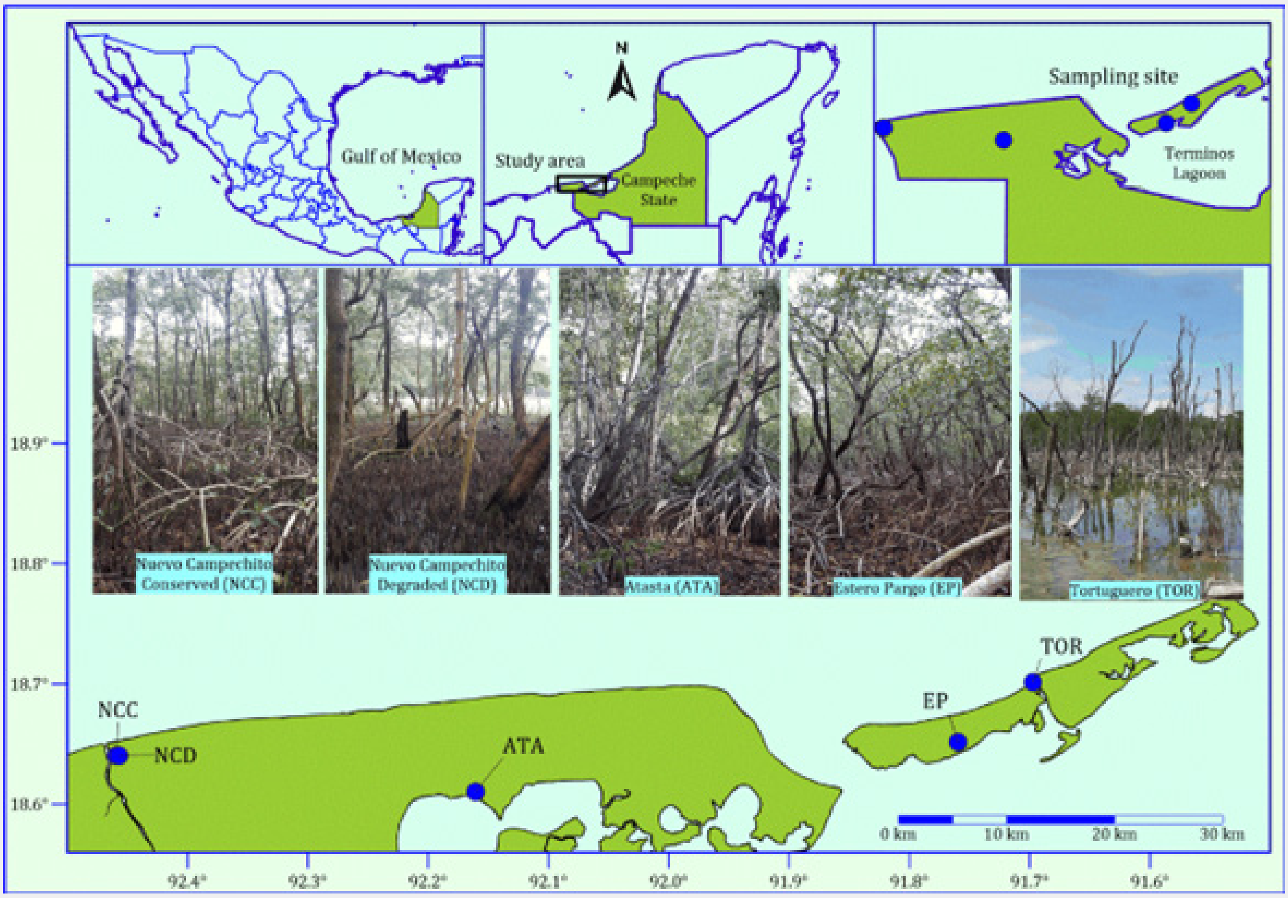

Figure 1: Location of the study area and sampling sites with different conditions of ecological degradation in areas surrounding the Terminos Campeche lagoon

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Terminos Lagoon is surrounded by mangrove forest (*Rhizophora mangle, Avicennia germinans, Laguncularia racemos*a, and *Conocarpus erectus*), covering an area as large as the open-water area of the lagoon. Therefore, mangrove constitutes a significant component of this ecosystem. The climate of the coastal plain of the Gulf of Mexico has four seasons: dry from February to April, transition in May, wet from June to September, and *nortes* from October to March [15]. In the Gulf of Mexico, the windy season is locally called *nortes* and is associated with low temperatures, northerly winds up to 100km h^{-1}, and rainfall. The annual precipitation fluctuates between 1200 and 1650mm. The annual temperature varies between 17°C and 37°C.

We considered the dry, rainy and *nortes* seasons on the sampling campaigns. Field work was conducted during March and June 2019 and January 2020. The study covered five mangrove sites with different conditions of ecological degradation: Atasta (ATA), Estero Pargo (EP), Nuevo Campechito conserved (NCC) and Nuevo Campechito degraded (NCD). On the *nortes* and rainy seasons we also sampled at Tortuguero (TOR).

The mangrove's ecological condition was classified as good or conserved, fair and poor. A conserved site refers to a mangrove forest that is in natural condition, with high vegetation density with heights ranging from 4 to 8m. The fair condition refers to vegetation with heights varying from 1 to 2m, with degraded mangrove or natural regeneration of mangrove. Poor condition refers to dead and degraded mangroves. The location and characteristics of each monitoring site are presented in Figure 1 & Table 1.

Table 1: Location of sampling sites and their ecological condition.

Mangrove	Location		Mangrove Species	Mangrove Condition
	N	W		
Atasta (ATA)	18°36'38.22"	92°9'39.06"	*Rhizophora mangle* *Laguncularia racemosa*	Good-Conserved
Estero Pargo (EP)	18°39'6.07"	91°45'34.12"	*Rhizophora mangle* *Laguncularia racemosa*	Good-Conserved
Nuevo Campechito Conserved (NCC)	18°38'24.8"	92°27'33.7"	*Avicennia germinans* *Rhizophora mangle* *Laguncularia racemosa*	Good-Conserved
Nuevo Campechito Degraded (NCD)	18°38'26"	92°27'26"	*Avicennia germinans* *Laguncularia racemosa*	Fair-Degraded
Tortuguero (TOR)	18°42'05"	91°41'50"	*Mangrove logs only*	Dead-Degraded

Greenhouse gas samplings and flux measurements

At each mangrove site, a 4 x 12m plot was established considering free access to the zone, risks, mangrove vegetation structure and distribution. Closed chambers collected CO_2, CH_4, and N_2O from the sediment-atmosphere interface. Three chambers sampled at each site. The chambers consisted of a PVC pipe (diameter 19.5cm, length 14.5cm, volume 4.33L and area of 0.029m^2). The open end of the chambers was inserted 3cm into the soil. The deployment time was set at 80min with a sampling of 20 minutes intervals. The chambers have a port which uses an injection septum for gas chromatography, and with a *vacutainer* needle sampled 20ml in headspace-type vials, previously evacuated in the laboratory at approximately -500mbar.

The samples were analyzed with a gas chromatographer Shimadzu model GC-2014AFsc coupled to a methanizer with flame ionization detector (FID), with a Hayesep D column of 80/100 13 ft X 1/8 in. The carrier gas was N_2 5.0 UHP at 25ml min^{-1}. The instrument operated under isothermal conditions (80° C). For the calibration curves we employed certified standard of CH_4, CO_2 and NO_2 at 500, 6161 and 5ppmv respectively in nitrogen balance. Analytical uncertainty was ± 5%.

GHG flux was calculated with a linear regression of gas concentration in the chamber over time. Only regressions with r^2 values ≥ 0.8 were used for flux calculations from all gases and all sites following Howard et al. [16]. GHG efflux rate (Fx) was calculated as:

$$Fx = (P \times V) \times \frac{\Delta GHG}{\Delta t} / (R \times S \times T) \qquad (1)$$

where *P* is the atmospheric pressure (assume the value = 1 atmosphere), *V* is the volume of the chamber (L), *R* is the ideal gas constant = 0.0820 (L*atm/K*mol) , *S* is the surface area covered by each chamber (m^{-2}), *T* is the temperature in Kelvin degrees at the time of each measurement (K= 273 + temp in °C), and *ΔGHG/Δt* is the change in GHG concentration over time (Δt) based on the slope of linear regression.

Based on the average gas fluxes of the different mangrove zones, the CH_4 and N_2O were converted to CO_2-equivalent (CO_2-eq) to indicate the gas warming effect [17]. The CO_2-equivalent flux was calculated using the following formula:

$$CO_2\text{-}eq\left(Mg\ ha\ yr^{-1}\right) = FGHI \times GMP \qquad (2)$$

where *FGHI* are annual fluxes of CO_2, CH_4, and N_2O between terrestrial and atmospheric ecosystems as a function of C and N mass, *GMP* is the warming effect or the conversion of CO_2, CH_4 and N_2O emissions to CO_2 equivalents as 1, 27 and 273, respectively, over a 100-year timeframe [17].

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Sampling and analyses of soils

To determine the physicochemical properties of the soils, we plot three sampling points of 1m^2 at each mangrove and took four soil core samples at 0-30 and 30-60cm depth using a sampler of 193.3cm^3. In total 84 samples.

The samples were stored in plastic bags and transported to the laboratory. Soil samples were dried at room temperature, pulverized, and passed through a 2mm sieve. All field samples were processed following standard protocols for quantifying mangrove soils. All visible organic matter (roots, pneumatophores and leaves) were removed from the soil samples prior to further analysis. The temperature of soil (Ts) was determined *in situ*, using a Redox ORP 14 electrode (220mV/pH7) connected to a pH/mV/T meter PCE-228. The sediment sample was diluted with distilled water 1:5, and then the probe was inserted into the cleared solution to measure the redox potential (E_h).

Soil moisture (SM) was determined according to Etchevers et al. [18]. The pH was determined with a HANNA (Instruments electronic) model pH211. The pH meter was calibrated with two buffer solutions 7 and 4 Merck Certipur (DEU). The soil electrical conductivity (EC) was measured using a TRANS instrument model HC3010, TDS-Conductivity-Salinity (USA), with an electrode TIPB10-0400 with K = 0.9660 and calibrated with a standard solution of 1.4mS. The pH and EC were measured from aqueous extracts and verified in duplicate after 1min, followed by stirring of samples for 30s. The aqueous extracts were prepared with deionized water (>18.2 MΩcm) and $CaCl_2$ 0.01 M ACS certified (Japan) ($CaCl_2 \cdot 2H_2O$, Fisher Scientific, Hampton, NH, USA) solution. The determination of soil texture was made following Bouyouco's method [19]. For bulk density (BD), an undisturbed sample of soil was taken using a steel cylinder (95.4cm^3). BD was determined from the oven-dried (105°C) mass of the core and the core volume.

We analyzed Cl^-, $NO_3^{\ -}$ and $SO_4^{\ 2-}$ by anion exchange chromatography, applying the high-resolution liquids chromatography technique (HPLC).

Soil organic matter percentage (SOM) was quantified using the loss on ignition (LOI) method [20]. The determination of soil organic carbon percentage (SOC) was calculated using the equation proposed by Kauffman & Donato [21]:

$$\%SOC = (0.415 \times \%SOM) + 2.89 \qquad (3)$$

The soil carbon stock (SCS) per sampled depth interval was calculated according to Kauffman & Donato [21]:

$$Soil\ Carbon\ Stock\left(Mg \cdot ha^{-1}\right) = BD \times SDI \times \%SOC \qquad (4)$$

where BD is the bulk density (g·cm^{-3}) and SDI is the soil depth interval (cm). The total SCS by site was calculated with the C stocks of both soil depth ranges (0-30 and 30-60cm).

Statistical analysis

The assumption of normality and homogeneity of variances was tested using the Shapiro–Wilk and Levene tests. The data did not have a normal distribution, so we applied the Kruskal-Wallis test. This analysis determined the differences in greenhouse gas fluxes and sediment physicochemical properties among sampling seasons and mangrove sites. If the difference was significant at $p < 0.05$, then a post-hoc Bonferroni test was used to determine the difference. We used multivariate principal component analysis (PCA) to assess the relationships between sediment properties and GHG as well as the two ecological conditions (conserved vs degraded mangroves). Statistical analysis was conducted using SPSS Statistics v27.0 (SPSS Inc., Armonk, New York).

Results and Discussion

Seasonal variability of CO2, CH4 and N2O fluxes at the sediment-air interface and their physicochemical drivers

Based on the Kruskal-Wallis test, CO_2, CH_4, and N_2O fluxes varied significantly between sampling periods ($p < 0.05$).

Carbon dioxide fluxes

CO_2 flux ranged between 184.8 to 1682.3mg m^{-2} h^{-1}. CO_2 fluxes from mangroves studied in southern China have ranged from 0 to 904.6mg m^{-2} h^{-1} [22-26], Can Gio mangrove in Vietnam presented CO_2 fluxes from 234.1 to 953.3mg m^{-2} h^{-1} [27] and New Caledonia 57.4 to 389.4mg m^{-2} h^{-1} [28-30].

The highest fluxes of CO_2 (1209.3 ± 297.1mg m^{-2} h^{-1}) in this study were recorded in the dry and warm seasons, under conditions of low humidity and high soil temperature (Table 2). The lowest fluxes (459.0 ± 154.2mg m^{-2} h^{-1}) were in *nortes* season (Figure 2A). A high CO_2 flux to the atmosphere with warmer temperatures was consistent with other studies in mangroves [31,32]. A high temperature in the mangrove soil led to an increase in microbial activity which generates higher levels of soil respiration and CO_2 emissions [33,34]. Also, the rise in temperature accelerates the decomposition of organic matter and consequently produces and emits CO_2 [35].

During the dry and warm seasons, the soils were never flooded and according to Chen et al. [22] and Alongi [36], CO_2 emission rates from mangrove soil tend to be higher when soils are exposed to the atmosphere, because molecular diffusion is faster for gases than for fluids, increasing the aerobic respiration and accelerating chemical oxidation of soil organic matter. When the temperature decreased during the *nortes* season, CO_2 emissions from mangrove soils also dropped. During the rainy season, low CO_2 fluxes were observed despite the temperatures were around 26.6 to 27.2°C, so precipitation may influence the fluxes [27]. In flooded soils, anoxic conditions can be induced by limiting the decomposition processes of organic matter, hence CO_2 production diminishes [37].

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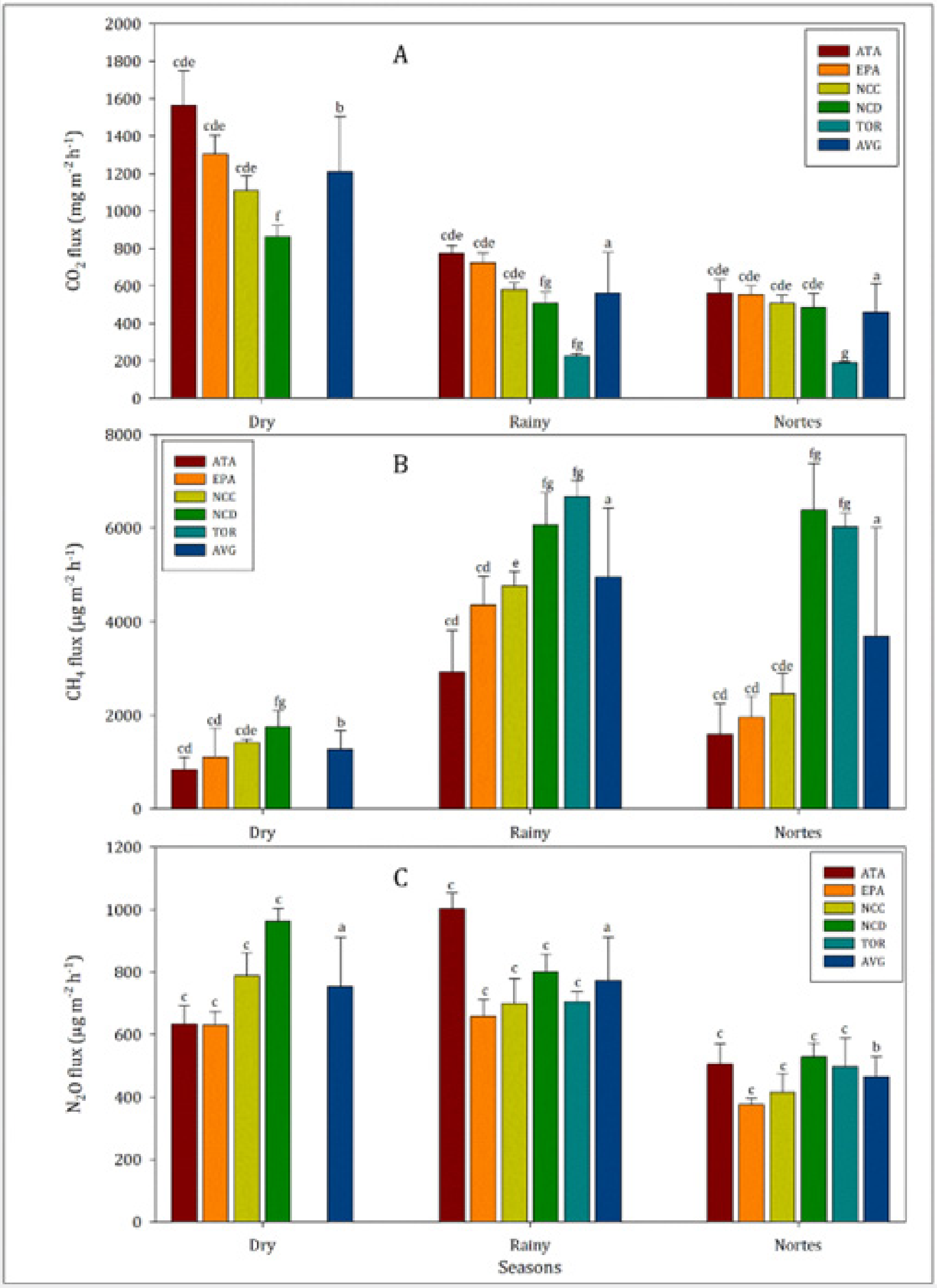

Figure 2: Greenhouse gas fluxes for the three seasons (dry, rainy and norths) at the different mangrove's sites, Atasta (ATA), Estero Pargo (EP), Nuevo Campechito conserved (NCC), Nuevo Campechito degraded (NCD), and Tortuguero (TOR): A) carbon dioxide fluxes, b) methane fluxes, c) nitrous oxide fluxes.

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Table 2: Soil summary values of the soil profile (0-60cm) at different mangrove sites and seasons. Soil temperature (Ts), the redox potential (Eh), soil moisture (SM), pH, electrical conductivity (EC), bulk density (BD), soil organic matter (SOM) and soil organic carbon (SOC). Mean and standard deviation are given. Letters indicate a significant difference between sites (p<0.05) according to Bonferroni test.

Depth	Season	Sites	Ts (°C)	E_h (mV)	SM %	pH	EC (ds m^{-1})	BD (g cm^{-3})	SOM %	SOC %
0-30cm	Dry	ATA	27.3 ± 0.9^{b}	126 ± 8.4^{a}	47.7 ± 1.6^{c}	8.1 ± 0.02^{a}	35.3 ± 5.5^{ab}	0.9 ± 0.2^{b}	13.2 ± 0.2^{a}	8.4 ± 0.2^{a}
		EP	28.1 ± 0.8^{a}	94 ± 3.3^{b}	59.0 ± 3.7^{c}	6.2 ± 0.06^{c}	41.0 ± 7.0^{a}	1.1 ± 0.2^{a}	9.6 ± 1.0^{b}	6.9 ± 0.1^{b}
		NCC	27.8 ± 0.5^{b}	84 ± 13.9^{b}	45.2 ± 1.6^{c}	7.0 ± 0.04^{b}	33.3 ± 0.1^{b}	1.1 ± 0.3^{a}	8.3 ± 0.3^{b}	6.3 ± 0.3^{b}
		NCD	29.2 ± 0.8^{a}	83 ± 10.5^{b}	63.3 ± 2.8^{bc}	7.2 ± 0.02^{b}	32.2 ± 4.3^{b}	0.7 ± 0.1^{b}	4.8 ± 0.1^{c}	4.9 ± 0.1^{c}
	Rainy	ATA	27.1 ± 0.1^{ab}	-116 ± 23.3^{c}	70.1 ± 7.0^{ab}	6.2 ± 0.05^{c}	34.2 ± 2.2^{b}	1.1 ± 0.2^{a}	16.4 ± 0.5^{a}	9.7 ± 0.2^{a}
		EP	26.6 ± 0.4^{ab}	-105 ± 20.4^{c}	72.6 ± 6.3^{ab}	6.9 ± 1.03^{bc}	32.3 ± 4.0^{b}	1.0 ± 0.1^{a}	14.5 ± 1.3^{a}	8.9 ± 0.2^{a}
		NCC	27.2 ± 0.1^{ab}	-108 ± 2.1^{c}	81.5 ± 1.1^{a}	6.9 ± 0.07^{bc}	33.3 ± 2.1^{b}	1.1 ± 0.6^{a}	9.3 ± 0.7^{b}	6.7 ± 0.1^{b}
		NCD	27.0 ± 0.2^{ab}	-190 ± 19.8^{d}	83.3 ± 1.2^{a}	7.5 ± 0.01^{ab}	20.2 ± 2.6^{d}	1.0 ± 0.1^{a}	4.4 ± 0.1^{bc}	4.7 ± 0.1^{b}
		TOR	26.8 ± 0.2^{ab}	-182 ± 18.7^{d}	85.0 ± 4.2^{a}	7.3 ± 0.02^{b}	30.0 ± 7.0^{c}	0.9 ± 0.2^{b}	3.5 ± 0.2^{bc}	4.3 ± 0.2^{b}
	Nortes	ATA	23.4 ± 0.2^{c}	-131 ± 8.0^{c}	73.6 ± 5.5^{ab}	6.9 ± 0.02^{bc}	37.3 ± 1.7^{a}	1.1 ± 0.1^{a}	14.8 ± 0.2^{a}	9.0 ± 0.4^{a}
		EP	23.9 ± 0.6^{c}	-170 ± 12.4^{cd}	79.9 ± 6.1^{ab}	6.3 ± 0.09^{c}	32.1 ± 4.3^{b}	1.0 ± 0.2^{a}	13.8 ± 0.4^{a}	8.6 ± 0.4^{a}
		NCC	24.0 ± 0.6^{bc}	-128 ± 8.08^{cd}	81.2 ± 8.1^{a}	6.5 ± 0.04^{c}	35.2 ± 0.1^{b}	0.9 ± 0.0^{b}	9.4 ± 0.4^{b}	6.8 ± 0.2^{b}
		NCD	24.0 ± 0.8^{bc}	-195 ± 26.1^{d}	83.2 ± 3.8^{a}	7.8 ± 0.05^{ab}	30.2 ± 6.7^{c}	1.1 ± 0.0^{a}	4.1 ± 0.3^{c}	4.6 ± 0.3^{b}
		TOR	26.7 ± 0.8^{ab}	-189 ± 23.5^{d}	82.9 ± 8.0^{a}	7.2± 0.0^{b}	31.0 ± 2.9^{bc}	0.8 ± 0.1^{b}	3.1± 1.1^{c}	4.2 ± 0.1^{b}
30-60cm	Dry	ATA	24.0 ± 0.1^{a}	90 ± 8.1^{ab}	62.3 ± 3.8^{bc}	5.8 ± 0.04^{d}	34.0 ± 2.6^{b}	1.3 ± 0.9^{a}	10.4 ± 0.8^{a}	7.2 ± 0.9^{ab}
		EP	26.9 ± 0.2^{ab}	55 ± 4.9^{a}	65.0 ± 4.7^{bc}	5.1 ± 0.09^{d}	38.9 ± 7.4^{a}	1.2 ± 0.6^{a}	9.2 ± 0.6^{b}	6.7 ± 0.5^{b}
		NCC	26.8 ± 0.5^{ab}	100 ± 10.5^{a}	30.8 ± 5.6^{c}	7.5 ± 0.02^{b}	31.2 ± 1.3^{bc}	1.3 ± 0.3^{a}	6.7 ± 0.8^{bc}	5.7 ± 0.8^{b}
		NCD	26.7 ± 0.2^{ab}	132 ± 16.2^{a}	24.6 ± 2.2^{c}	8.4 ± 0.09^{a}	30.0 ± 4.3^{c}	1.1 ± 0.5^{a}	4.6 ± 0.9^{c}	4.8 ± 0.9^{c}
	Rainy	ATA	26.9 ± 0.3^{ab}	-159 ± 20.1^{cd}	80.5 ± 7.0^{a}	6.5 ± 0.05^{c}	31.0 ± 3.2^{bc}	1.3 ± 0.6^{a}	11.1 ± 0.9^{a}	7.5 ± 0.7^{ab}
		EP	26.0 ± 0.8^{ab}	-115 ± 12.3^{c}	68.8 ± 5.4^{ab}	6.7 ± 0.08^{bc}	30.3 ± 4.5^{c}	1.2 ± 0.1^{a}	9.1 ± 0.7^{b}	6.7 ± 0.9^{b}
		NCC	26.5 ± 0.3^{ab}	-128 ± 4.9^{c}	66.8 ± 4.1^{ab}	6.5 ± 0.12^{c}	32.1 ± 3.2^{bc}	1.0 ± 0.2^{a}	6.8 ± 0.5^{bc}	5.7 ± 0.8^{b}
		NCD	27.2 ± 0.2^{ab}	-178 ± 19.3^{cd}	69.0 ± 3.6^{ab}	7.5 ± 0.03^{b}	23.0 ± 2.9^{d}	1.1 ± 0.2^{a}	5.0 ± 0.8^{c}	5.0 ± 0.9^{bc}
		TOR	26.0 ± 0.4^{ab}	-168 ± 10.6^{cd}	89.0 ± 6.1^{a}	7.7 ± 0.02^{ab}	32.0 ± 9.3^{b}	1.0 ± 0.2^{a}	5.1 ± 0.7^{c}	5.0 ± 0.6^{b}
	Nortes	ATA	23.0 ± 0.2^{c}	-180 ± 15.3^{d}	84.5 ± 5.9^{a}	6.2 ± 0.06^{c}	30.0 ± 2.7^{c}	1.3 ± 0.2^{a}	15.5 ± 0.8^{a}	9.3 ± 0.7^{a}
		EP	23.0 ± 0.7^{c}	-156 ± 12.4^{cd}	75.7 ± 6.7^{ab}	6.1 ± 0.30^{c}	31.7 ± 4.2^{bc}	1.2 ± 0.2^{a}	14.1 ± 0.8^{a}	8.7 ± 0.7^{a}
		NCC	23.6 ± 0.3^{c}	-133 ± 8.1^{c}	68.5 ± 8.3^{ab}	6.0 ± 0.02^{c}	23.2 ± 6.2^{d}	1.0 ± 0.1^{a}	8.9 ± 0.5^{b}	6.6 ± 0.6^{b}
		NCD	23.4 ± 0.1^{c}	-226 ± 27.3^{e}	70.8 ± 4.1^{ab}	7.8 ± 0.04^{ab}	25.0 ± 6.9^{d}	1.0 ± 0.0^{a}	5.5 ± 0.3^{bc}	5.2 ± 0.3^{b}
		TOR	23.5 ± 0.7^{c}	-173 ± 18.6^{cd}	79.3 ± 9.0^{ab}	7.1 ± 0.01^{b}	28.7 ± 5.1^{cd}	1.0 ± 0.1^{a}	4.6 ± 0.5^{bc}	4.8 ± 0.5^{b}

Methane fluxes

CH_4 fluxes ranged between 592.8 to 8909µg m^{-2} h^{-1} which were lower than those recorded in the mangroves of Shenzhen and Hong Kong in South China ranging from 0 to 82916µg m^{-2} h^{-1} [22-24]. The measured fluxes were similar to those recorded at the Bhitarkanika mangrove in India (2300µg m^{-2} h^{-1}) [38], Taiwan (5071.1µg m^{-2} h^{-1}) [39] and Jiulong River, China (5360.1µg m^{-2} h^{-1}) [24], but higher than some mangroves in New Caledonia, Brazil, and Indonesia [28,40,41].

The CH_4 fluxes were significantly higher in the rainy (4957.2 ± 1478.7µg m^{-2} h^{-1}) and *nortes* seasons (3688 ± 2325.3µg m^{-2} h^{-1}), and lower fluxes were observed during the dry season (1278 ± 393.9µg m^{-2} h^{-1}) (Figure. 2B). The CH_4 dynamics recorded in the Terminos lagoon was like other studies that attribute the variation of CH_4 emissions to sediment temperature and water level [42].

According to Chauhan et al. [38] sediment temperature is responsible for the seasonal variation of CH_4 emission. By decreasing the temperature, the decomposition of organic matter is reduced, producing methanogens. Methanogenic bacteria are responsible for releasing CH_4 and are active anaerobes in flooded and swampy areas [43,44]. It has been reported that the microbiological process that generates the formation of methane

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in the soil is controlled by edaphic factors among them, the redox potential (Eh) and the pH of the soil. The Eh during the rainy and northern seasons were from -105 to -205mV in the upper layer (0-30cm depth) and from -115 to -226 in the 30-60cm in the bottom layer (Table 2). A redox potential of -150 to -200mV favors methanogenesis in the natural wetlands which might have resulted in higher fluxes of methane [45]. pH ranged from 6.2 to 7.8 and are considered optimal for methane production [46].

High organic matter content and low Eh indicate that the degradation of more organic matter content induces greater CH_4 production, while high Eh indicates that the soil has adequate ventilation, conducting soil respiration and CO_2 emission [33].

Nitrogen oxid

N_2O fluxes varied significantly between sampling seasons (375.4 to 1002.2µg m^{-2} h^{-1}) but were in the range of reports from other authors [47,48]. The N_2O flux was higher in the rainy season (772.9 ± 138.5µg m^{-2} h^{-1}) and lower in *nortes* season (464.2 ± 65.4µg m^{-2} h^{-1}; Figure 2C). The seasonal variation of N_2O is like that recorded by Allen et al. [49] who identified that sediment temperature and moisture are the key to seasonal differences in N_2O fluxes.

Global warming potential

The CO_2-eq emission rate was 86.9 ± 31.7 Mg CO_2-eq ha^{-1} yr^{-1} with a contribution of 71.6% CO_2, 10.3% CH_4, and 18.1% N_2O. It had significant differences between seasons ($p < 0.001$). The CO_2-eq was higher in the dry season (Figure 3). There was also a significant difference between sites ($p = 0.01$), the ATA and EP mangroves contributed with 26.2% and 23.4% of the CO_2-eq respectively. The highest contribution to global warming potential among season and sites was CO_2 (62.2 ± 34.1 Mg CO_2-eq ha^{-1} yr^{-1}) followed by N_2O (15.7 ± 4.5 Mg CO_2-eq ha^{-1} yr^{-1}) and CH_4 (9 ± 5.7 Mg CO_2-eq ha^{-1} yr^{-1}). The CO_2-eq contribution has been observed in other studies [50-52]. Allen et al. [53] mention that in subtropical mangrove sediments during low CH_4 emissions, the N_2O has a high global warming potential that can dominate trace gas emissions, that pattern coincides with our results (Figure 3).

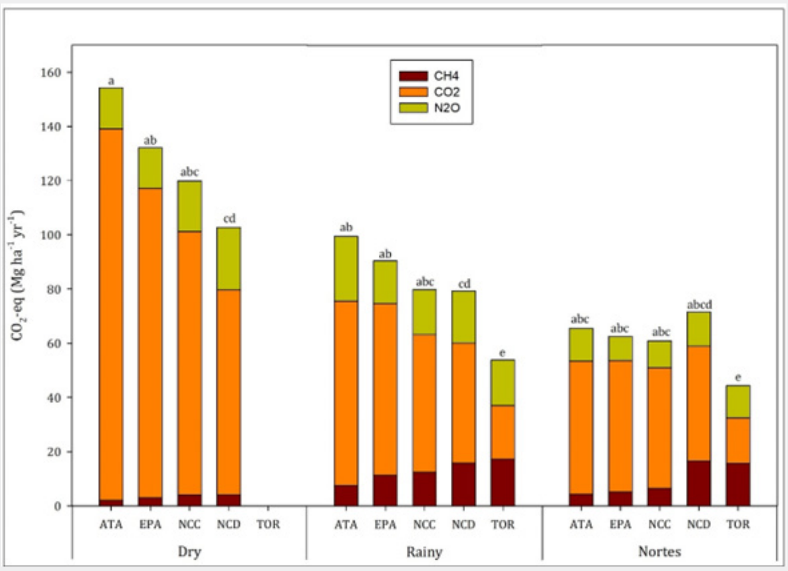

Figure 3: Total emissions expressed as CO2-equivalents according to their GWP over a 100-year timeframe (CH4: 27; CO2: 1; N2O: 273; IPCC, 2021) from different mangrove sites on each season.

Regardless of the cause, the loss of mangroves leads to a decrease in the organic carbon inventory, especially if the soil horizon is disturbed, which can be converted into CO_2-eq emissions to the atmosphere [54]. The CO_2-eq observed in the degraded mangroves (NCD and TOR) was 70.3 ± 22.8 Mg CO_2-eq ha^{-1} yr^{-1}, where the contribution of CO_2 was 56%, N_2O 23.8% and CH_4 19.8%; Thus, in degradation conditions, the emission of N_2O and CH_4 increases and that of CO_2 decreases.

GHG fluxes in conserved and degraded mangroves

The ecological condition of each mangrove affects the GHG fluxes. CO_2 and CH_4 fluxes had significant differences ($p < 0.05$) between conserved and degraded mangroves. ATA had the highest flux of CO_2 (966.4 ± 528.1mg m^{-2} h^{-1}), followed by the EP (859.8 ± 393.0mg m^{-2} h^{-1}). TOR had the lowest CO_2 fluxes (206.8 ± 24.9mg m^{-2} h^{-1}) (Figure 2A). The highest CH_4 fluxes were measured in NCD (4736.1 ± 2588.4µg m^{-2} h^{-1}) and TOR (6354 ± 453.7µg m^{-2} h^{-1}) which have an important degradation. N_2O did not show significant differences ($p > 0.05$), ATA had 713.6 ± 258.1µg m^{-2} h^{-1}, NCD 763.9 ± 219.6µg m^{-2} h^{-1} and NCC 634 ± 194.7µg m^{-2} h^{-1}. So, the highest CO_2 fluxes were measured in conserved mangroves, and the lower in degraded mangroves. The state of the mangrove (conserved or degraded) is observed in the PCA of Figure 4. The first two axes explained 72.5% of the variance, in PC1 the factors with the greatest contribution were NO_3^-, soil organic matter (SOM) and Eh. In PC2 were EC, Ts, and SO_4^{2-}. The sediments

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presented groups related to GHG emissions. That is, the PCA showed that the conserved mangroves were grouped because they have high values of CO_2, N_2O, Ts, EC, Eh, NO_3^-, and SOM. The degraded mangroves had relevant values of CH_4, pH, and SM, and poor values of SO_4^{2-}.

At ATA, EP, and NCC the concentration of SO_4^{2-} ranged between 16 and 36mg kg^{-1} and the NO_3^- between 30 and 66mg kg^{-1}. The SOM registered values between 9.3 - 16.4% (Table 2). *Rhizophora mangle* and *Laguncularia racemosa* dominate in ATA and EP and have a large leaf litter cover which is essential in the nutrient cycle, since its production and decomposition represents the main transfer of organic matter and nutrients from the aerial part to the surface of the soil [55,56]. Soils with litter produce carbon-rich compounds that are more susceptible to bacterial decomposition [57]. Microorganisms promote the decomposition of organic matter by nitrogen fixation, the reduction of sulfates and the production of enzymes [58]. In NCC, *Avicennia germinans* dominates the area, which has pneumatophores that allow the exchange of oxygen and CO_2 from the root system of the plant. Troxler et al. [59] mentions that black mangrove pneumatophores also contribute more average flux of CO_2 from the soil to the atmosphere.

Soil microorganisms, respiration of plant root cells and the degradation of leaf litter produce CO_2 [60]. The emission of CO_2 to the atmosphere occurs when microorganisms oxidize organic C using O_2, NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-} as electron acceptors [40,61]. The correlation of SOM, nutrients and high CO_2 emissions is related to site-specific conditions and biotic and abiotic factors. Hien et al. [35] mention that the development of mangroves and the enrichment of organic matter in the sediments also influences the properties of the sediment, modifying the production and emission of CO_2. Mangrove disturbance can also alter natural soil SOM decomposition and storage processes. When mangroves degrade the SOM can become mineralized, contributing to more CO_2 emissions [62].

NCD and TOR had the highest CH_4 fluxes. These sites show a negative correlation between CH_4 and Eh, SO_4^{2-}, and EC, and positive with pH (Figure 4). High values of salinity and SO_4^{2-} favor the activity of sulfate-reducing bacteria and hinder the metabolism of methanogens, since they inhibit the production of CH_4 from wetlands [63,64]. Methanogens are anaerobic and for methanogenesis to occur the redox potential must be as low as -200mV, and other competing terminal electron acceptors must have been reduced (O_2, NO_3^-, and SO_4^{2-}) [65]. Previous studies have found that the CH_4 potential soil production and anaerobic and aerobic oxidation have a negative correlation with soil redox potential [66] and with high salinity concentrations [38,45]. On the other hand, a pH of 7.6 facilitates the growth of methanogens and the production of CH_4 [38]. Other authors have also reported that in sites with loss of vegetation the flux of CH_4 increases considerably compared to pristine sites [50].

Soil N_2O flux did not present a clear pattern between conserved and degraded mangroves and no significant differences were observed ($p = 0.149$). ATA and NCC had the highest N_2O fluxes in the dry season and NCD the highest in the rainy season (Figure 2C). ATA and NCC had positive correlations of N_2O with Eh, NO_3^-, and EC; while NCD recorded negative correlations of N_2O with Eh, NO_3^-, and EC (Figure 4). Eh was positive in dry conditions and negative in rains and *nortes*; so, changes in the hydrological regime influence soil redox conditions and can alter nitrogen availability [67,68].

Nitrogen oxide emissions from soils are related to microbial processes of nitrification (oxidation of NH_4^+ to NO_2^- and NO_3^-) and denitrification (reduction of NO_3^- and NO_2^- to NO, N_2O and N_2) [69]. Both processes use soil mineral nitrogen (NH_4^+ and NO_3^-) that originate mainly from the mineralization of organic matter or fertilization.

In dry conditions, denitrification under aerobic environments carried out by chemolithotrophic nitrifying bacteria with positive Eh oxidizes NH_4^+ to NO_3^- and dominates the production of N_2O [70]. While in rains and *nortes*, under anaerobic conditions, the sediment had high levels of nitrates and negative Eh in the conserved sites (Table 2 & 3) that allows denitrification.

Table 3: Soil summary anions values of the soil profile (0-60cm) at different mangrove sites and seasons. Mean and standard deviation are given. Letters indicate a significant difference between sites ($p<0.05$) according to Bonferroni test.

Depth	Season	Sites	SO_4^{-2}(mg kg^{-1})	Cl-(mg kg^{-1})	NO_3-(mg kg^{-1})
0-30cm	Dry	ATA	36 ± 0.1^a	14 ± 0.0^{bc}	40 ± 0.7^a
		EP	31 ± 0.2^a	21 ± 0.1^{ab}	36 ± 0.1^a
		NCC	18 ± 0.2^c	20 ± 0.3^b	31 ± 0.3^a
		NCD	29 ± 0.2^{ab}	39 ± 0.2^a	26 ± 0.7^{ab}
	Rainy	ATA	26 ± 0.1^b	14 ± 0.0^{bc}	36 ± 0.8^a
		EP	20 ± 0.1^{bc}	25 ± 0.1^a	37 ± 0.4^a
		NCC	21 ± 0.1^{bc}	23 ± 0.0^{ab}	38 ± 0.4^a
		NCD	13 ± 0.1^c	21 ± 0.2^{ab}	19 ± 0.2^b
		TOR	16 ± 0.2^{bc}	30 ± 0.2^a	20 ± 0.8^b

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	Nortes	ATA	29 ± 0.2^{ab}	13 ± 0.0^{bc}	40 ± 0.9^{a}
		EP	21 ± 0.2^{b}	27 ± 0.2^{a}	33 ± 0.2^{a}
		NCC	23 ± 0.3^{b}	29 ± 0.2^{a}	31 ± 0.2^{a}
		NCD	15 ± 0.1^{c}	26 ± 0.1^{a}	18 ± 0.8^{b}
		TOR	10 ± 0.1^{c}	30 ± 0.3^{a}	19 ± 0.9^{b}
30-60cm	Dry	ATA	34 ± 0.3^{a}	10 ± 0.2^{c}	32 ± 0.8^{a}
		EP	30 ± 0.2^{a}	22 ± 0.1^{ab}	29 ± 0.5^{a}
		NCC	20 ± 0.4^{bc}	25 ± 0.3^{a}	25 ± 0.4^{ab}
		NCD	21 ± 0.2^{bc}	32 ± 0.1^{a}	13 ± 0.9^{b}
	Rainy	ATA	20 ± 0.2^{c}	12 ± 0.2^{bc}	38 ± 0.6^{a}
		EP	23 ± 0.1^{b}	25 ± 0.1^{a}	39 ± 0.1^{a}
		NCC	16 ± 0.1^{bc}	21 ± 0.4^{ab}	31 ± 0.3^{a}
		NCD	12 ± 0.3^{c}	27 ± 0.4^{a}	15 ± 0.2^{b}
		TOR	11 ± 0.2^{c}	35 ± 0.1^{a}	12 ± 0.5^{b}
	Nortes	ATA	21 ± 0.5^{b}	10 ± 0.0^{c}	31 ± 0.4^{a}
		EP	22 ± 0.2^{b}	22 ± 0.4^{ab}	36 ± 0.1^{a}
		NCC	23 ± 0.2^{b}	21 ± 0.7^{ab}	30 ± 0.1^{a}
		NCD	15 ± 0.4^{c}	18 ± 0.3^{ab}	12 ± 0.2^{b}
		TOR	14 ± 0.7^{c}	30 ± 0.2^{a}	17 ± 0.5^{b}

Soil carbon stock

The mean SCS was not significantly different between climatic periods ($p = 0.88$) and between sampling depths ($p = 0.35$). The total soil carbon stock (0 - 60cm depth) was 431 ± 180.9 Mg C ha^{-1} during the *nortes*, 419 ± 142.8 Mg C ha^{-1} on the rainy and 415 ± 103.6 Mg C ha^{-1} on the dry seasons. In the upper layer (0-30cm), the mean was 201± 71.8 Mg C ha^{-1}, and for the 30-60cm layer was 221 ± 70.3 Mg C ha^{-1} (Figure 5). The carbon stored in mangrove soil is consistent with other studies carried out in Laguna de Terminos [71] and other places of Mexico [72], as well as other parts of the world [73], but higher than Sofala Bay [74]; Dominican Republic [75]; Florida [76] and Malaysia [77] (Table 4). Zamora et al. [12] quantified the carbon reservoir in Mexican coastal forested wetlands from 79 - 650 Mg C ha^{-1}. The observed differences are probably related to the measured soil depth.

Table 4: Comparison of mangrove ecosystem C stocks around the world with present study.

Site	Depth (cm)	Mangrove C Stocks (Mg C ha^{-1})	Source
Western sector of the coast of Campeche	0-30	251	This study
Western sector of the coast of Campeche	30-60	286	This study
Laguna de Términos, Campeche, Mexico	0-60	252	[71]
Central coastal plain of Veracruz, Mexico	0-60	375	[72]
Southeast of Iran	0-60	282	[73]
Florida	0-30	122	[76]
Malaysia	0-50	173	[77]

The ATA stores 591.3 ± 85.1, EP 516.3 ± 53, NCC 403.4 ± 23.5, NCD 287.9 ± 22.4 and TOR 255.8 ± 16.4 Mg C ha^{-1} reflecting different conditions of ecological degradation.

Soils showed an apparent density ranged between 0.7 - 1.1g cm^{-3} in the most superficial layer and 1.0 - 1.3g cm^{-3} in the 30 - 60cm layer (Table 2). Mitsch & Gosselink [65] mention that mineral soils have apparent densities ranged on 1 - 2g cm^{-3}, so it is likely that some horizons correspond to organic soils and the deeper layer to mineral soils.

The preserved mangroves had the highest SOM and SOC. The highest concentrations were observed in the rainy season (between 0 - 30cm) and *nortes* throughout the sediment column (0 - 60cm, Table 2). Those seasons had intense rains and tides that flooded the sites, the soil generates reserves of organic carbon due to the stagnant water for long periods, delaying the oxidation of SOM and increasing the accumulation rate of SOC due to the anaerobic conditions or a lower soil temperature relative to the ambient [78]. In the dry season, the low water content and CO_2 concentration of the soil reduce the stored carbon intensifying the flux of CO_2 [79].

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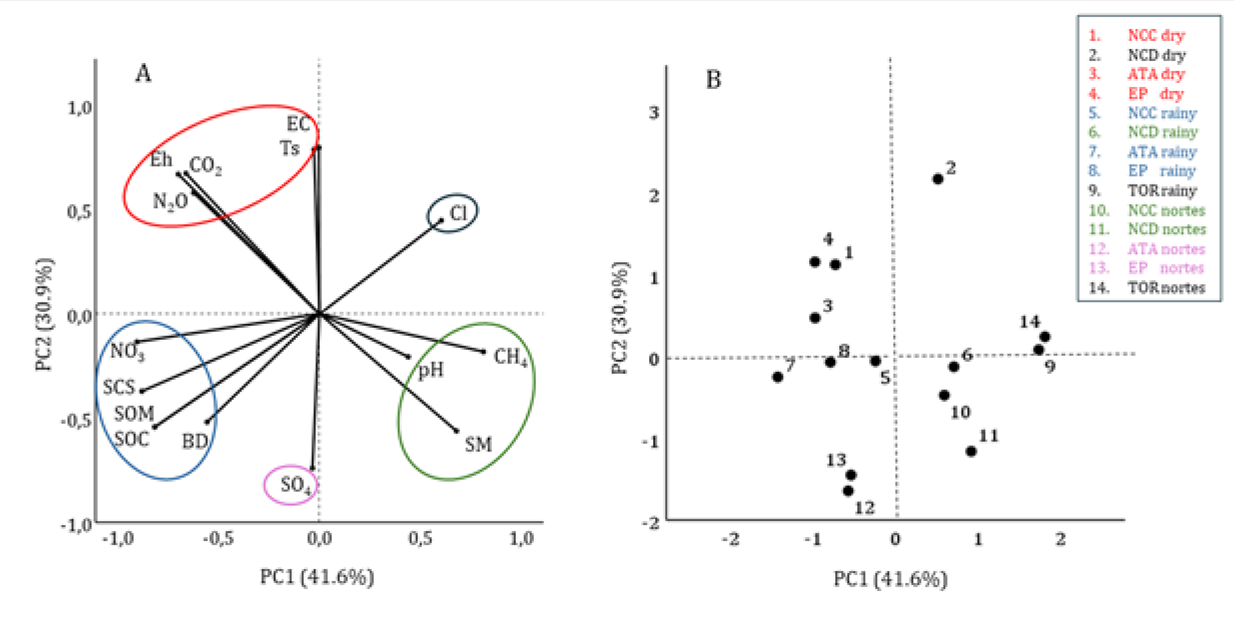

Figure 4: PCA carried out on the physicochemical parameters of the sediments of the preserved and degraded mangroves. (A) Correlation circles PC1 × PC2 of the variables corresponding to the physical-chemical parameters (the color of the circle represents the variables associated with each mangrove in the different epochs analyzed as indicated in the box on the right), (B) Factorial plane of the samples. Each point represents a specific mangrove and time.

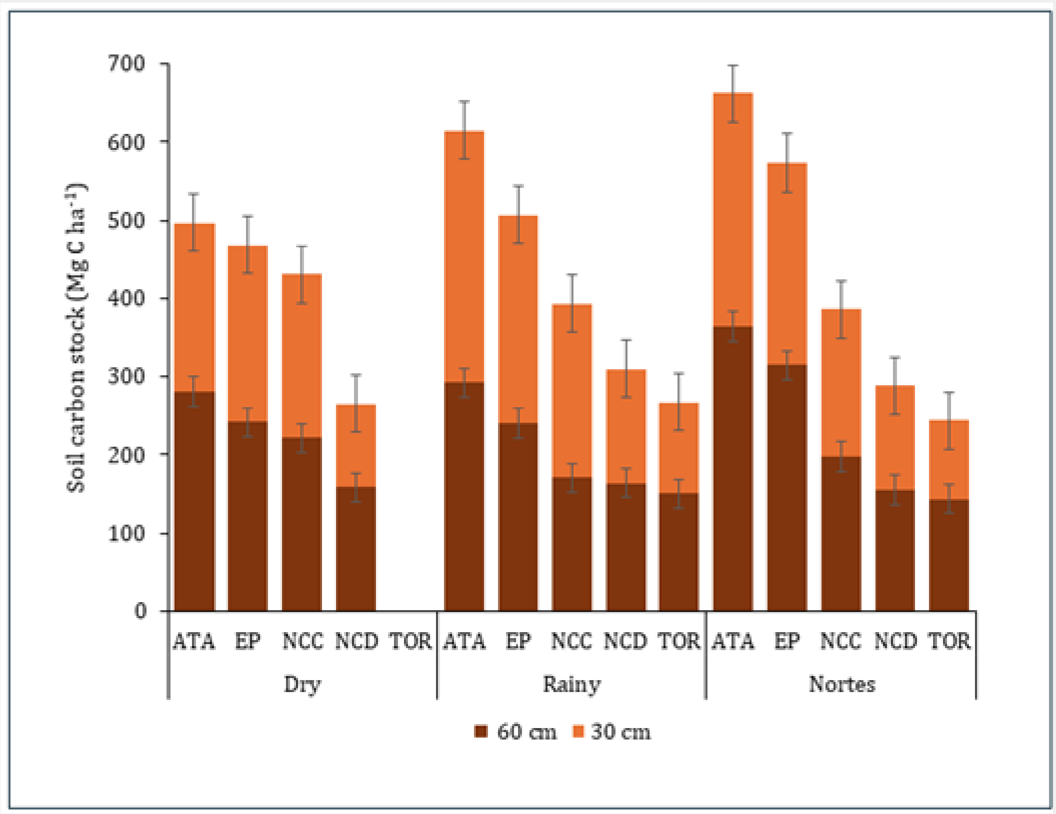

Figure 5: Soil carbon stock at 0-30cm and 30-60cm depth during dry, rainy and nortes seasons at the different mangrove's sites: Atasta (ATA), Estero Pargo (EP), Nuevo Campechito conserved (NCC), Nuevo Campechito degraded (NCD), and Tortuguero (TOR).

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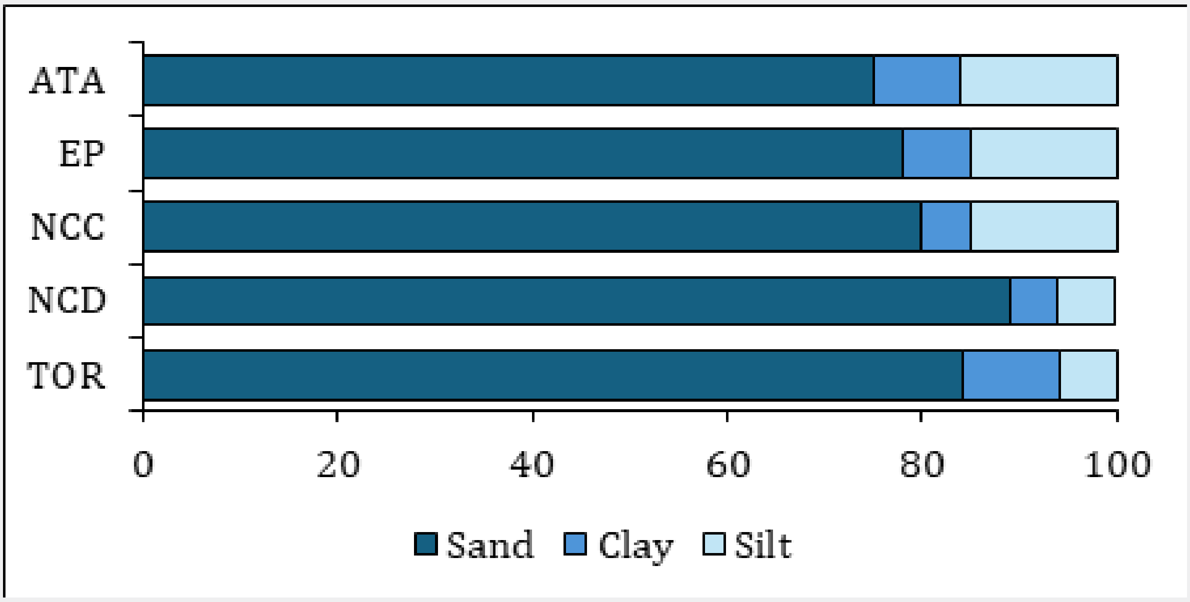

Figure 6: Soil particle size measured as a percentage contribution of sand, clay and silt at the different mangroves sites: Atasta (ATA), Estero Pargo (EP), Nuevo Campechito conserved (NCC), Nuevo Campechito degraded (NCD), and Tortuguero (TOR).

The percentage of sand ranged between 75 and 89%, clay 5 to 10% and silt 6 to 16%, fine sediments (clay + silt) were greater in conserved than degraded mangroves (Figure 6) and together with the sediment humidity influence the SCS, since the water content and the percentage of fine sediments have a positive impact on the surface SOC [80,81]. On the other hand, Schile et al. [82] mentions that the texture of the sediment is one of the factors that regulates the preservation of organic matter, which explains why carbon reserves are poor in sandy soils.

The results suggest that carbon storage is influenced by the ecological conditions of the sites that induce changes in soil properties such as moisture, texture, the amount of SOM, SOC, bulk density and soil depth (Figure 4).

Degraded sites have lower SCS in the 0 - 30cm layer of the sediment (Figure 5). According to Lovelock et al. [83] the disturbance and exposure of sediment in degraded mangroves accelerates the erosion of the upper layer, leaving it exposed to physical forces that lead to chemical weathering and higher decomposition rates, which leads to lower carbon storage. Senger et al. [10] found that carbon is rich in the upper 30cm of the sediment in intact sites and is poor in degraded sites. Likewise, intact plots have more SOC associated with higher CO_2 fluxes, while degraded plots have a higher SOC low and poorer CO_2 fluxes, which is like our results.

Degradation of mangroves leads to higher CO_2 emission and changes the status from carbon sink to carbon source [84] which significantly contributes to global warming and climate change.

Conclusion

GHG fluxes were directly related to seasonal variation and to environmental factors specific to each mangrove. Seasonality influenced soil conditions; flooded conditions favored CH_4 and N_2O production, while the dry season with more oxygenated soils favored CO_2 production. CO_2 and N_2O fluxes were higher in conserved sites controlled by redox potential, soil temperature and electrical conductivity, while CH_4 fluxes were higher in degraded mangroves controlled by pH, SO_4 and soil moisture. The highest carbon storage was observed in conserved mangroves. Ecological degradation in mangroves can increase GHG emissions and reduce the ecosystem's ability to store carbon. Therefore, mangrove conservation and restoration are essential to mitigate GHG emissions and maintain their function as carbon sinks.

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