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Greenhouse Gas Emissions from a Tropical Eutrophic Freshwater Wetland

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***Abstract*—**This study measured the fluxes of greenhouse gases (GHGs) i.e. CO_2, CH_4 and N_2O from a tropical eutrophic freshwater wetland ("Sonso Lagoon") which receives input loading nutrient from several sources i.e. agricultural run-off, domestic sewage, and a polluted river. The flux measurements were carried out at four different points using the static chamber technique. CO_2 fluxes ranged from -8270 to 12210 $mg.m^{-2}.d^{-1}$ (median = 360; SD = 4.11; n = 50), CH_4 ranged between 0.2 and 5270 $mg.m^{-2}.d^{-1}$ (median = 60; SD = 1.27; n = 45), and N_2O ranged from -31.12 to 15.4 mg N_2O $m^{-2}.d^{-1}$ (median = 0.05; SD = 9.36; n = 42). Although some negative fluxes were observed in the zone dominated by floating plants i.e. *Eichornia crassipes, Salvinia* sp., and *Pistia stratiotes* L., the mean values indicated that the Sonso Lagoon was a net source of CO_2, CH_4 and N_2O. In addition, an effect of the eutrophication on GHG emissions could be observed in the positive correlation found between CO_2, CH_4 and N_2O generation and COD, PO_4^{-3}, NH_3-N, TN and NO_3^-N. The eutrophication impact on GHG production highlights the necessity to limit the anthropic activities on freshwater wetlands.

***Keywords*—**Eutrophication, greenhouse gas emissions, freshwater wetlands, climate change.

I. Introduction

FRESHWATER Wetlands (FW) provide ecosystem services such as water purification, flood control, nutrient cycling, carbon sequestration, foods, maintenance of biodiversity and climate regulation [1], [2]. By contrast, FWs can be an important source of GHGs and it has been estimated that CH_4 emissions from tropical wetlands are 128 $Tg.yr^{-1}$ and equivalent to 75% of the total emissions from wetlands worldwide [3]. Wetlands can also emit between 0.01 and 1% of N_2O and 0.648-9.18 Tg C (CO_2) [4], whereas the global CO_2 evasion rates are 1800 Tg $C.yr^{-1}$ from streams and rivers and 320 Tg C. yr^{-1} from lakes [5]. These emissions can be even higher where wetlands have been affected by anthropogenic activities such as agricultural run-off and domestic sewage discharges. These activities provide input loading nutrients (N and P) and organic matter to FW, resulting in a severe alteration of the structure and function by eutrophication of these ecosystems [4]. Eutrophication in FW generally promotes excessive algae and plant growth and decay, favouring simple algae and plankton over other more complicated plants, and this causes a severe reduction in water quality i.e. oxygen depletion [6]. In addition, the nutrient loading enhances organic matter decomposition and microbial activity [7], which may lead to increased accumulation of carbon and nitrogen. So eutrophication affects the FW biogeochemistry, leading to acceleration of the exchange of GHGs between FWs and the atmosphere [8], [9].

Several authors have shown that freshwater ecosystems under eutrophication or with excessive loading nutrients are important sources of GHGs [8], [10]-[16]. Since these studies were carried out under temperate and subtropical conditions it is important to study whether the GHG emissions from these wetlands are comparable to those under tropical conditions and also whether the variables mentioned influence their GHG production.

In Colombia, approximately 20,000,000 hectares are classified as wetland and most of these wetlands are eutrophic. As a consequence, the GHG emissions are increasing. Because the impact of eutrophication on GHG emissions in tropical eutrophic wetlands is still unclear and there are many uncertainties about the magnitude of these GHG emissions, in this study we focus on (1) the quantification of CH_4, CO_2, and N_2O and (2) the identification of the factors that regulate the emissions of CH_4, CO_2, and N_2O from an eutrophic tropical FW.

II. Material and Methods

A. Study Area

The Sonso Lagoon (3°51′43.36′′ N and 76°20′57.12′′ W) is a shallow eutrophic lake. It is located in the southwestern part of Colombia, on the right bank of the Cauca River. The total area of the Sonso Lagoon is 20.5 km^2 of which 7.5 km^2 are water mirror and 13 km^2 riparian buffer zones. It has a mean depth of 1.6 m with a maximum depth of 3 m. The climate is tropical with a mean annual temperature ranging from 21 to 26°C and 1,375 mm precipitation yearly. The Sonso Lagoon exchanges water and sediments with the regional Cauca River through the Caño Nuevo Channel (Fig. 1). This river is characterized by high pollution due to industrial effluents. In addition, there are inlets of domestic sewage and agricultural runoff from sugar cane crops into the lake. Through these discharges, organic matter, nitrogen compounds, phosphorus compounds, heavy metals, pesticides and herbicides enter the lagoon affecting its water characteristics.

The four study sites in the Sonso Lagoon were as follows (Fig. 1): P1, exchange zone of water and sediments with the

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Cauca River; P2, zone dominated by domestic sewage and agricultural runoff discharges; P3, dominated by phytoplankton; P4, dominated by water hyacinths.

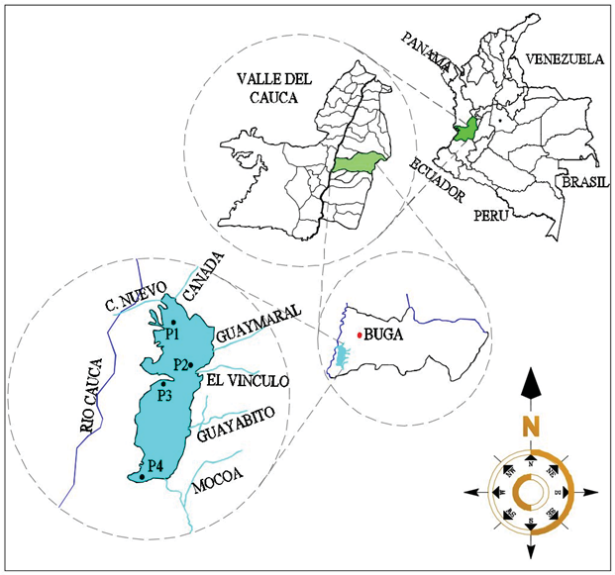

Fig. 1 Location of the Sonso Lagoon and sampling points for measurements of GHG emissions

B. Water Characteristics

Environmental data from the four sites of the Sonso Lagoon were collected to determine the water quality and to evaluate the relationship between GHGs and environmental parameters. The measurements of environmental data were carried out between 9 am and 3 pm, which coincided with the GHG emission measurements. Chemical oxygen demand (COD), total suspended solids (TSS), alkalinity, total Kjeldahl nitrogen (TKN), ammonium nitrogen (NH_4^+-N), and nitrate nitrogen (NO_3^--N) were measured according to Standard Methods [17]. Conductivity, pH, dissolved oxygen (DO), temperature and oxidation-reduction potential were measured with electrodes.

C. GHG Measurements

Emissions of CH_4, CO_2 and N_2O were estimated with the static chamber technique [18]. The static chambers were of propylene and cylindrical (Diameter 0.43 m and Height 0.26 m). The chambers were equipped with a sampling port having a rubber septum from which the gas sample was taken.

During measurements, the chambers were installed gently on the water surface of each point. The gas samples were taken at regular time intervals of 10 minutes (0, 10, 20 and 30 minutes). The sample was extracted by a 20 mL syringe, which was inserted at the point of making the chamber (rubber septum), after which the sample was removed and injected into a previously sealed vial and vacuum 10 ml.

The Flux of CH_4, CO_2 and N_2O were calculated according to the equation 1 from linear and no linear changes in the gas concentrations in the chamber headspaces [18].

$$F = \frac{dC}{dt_{t=0}} \times \frac{V_c}{A} \times \frac{1440\ min}{d} \quad (1)$$

F= Flux of CH_4, CO_2 y N_2O ($g.m^{-2}.d^{-1}$); $dC/dt_{t=0}$= Slope of the gas concentration curve ($g.m^{-3}.d^{-1}$); V_c= Volume of the chamber (m^3); A_c= The cross-sectional area of the chamber (m^2).

D. Gas Analysis

CH_4 was analyzed by gas chromatography (Shimadzu Co., Japan) equipped with a flame ionic detector (FID) and a Porapak Q column, and the temperature of the oven and injector ports were set at 60 and 80 °C, respectively. CO_2 was measured by an infrared spectrophotometer Qubit S151 CO_2 analyser (Loligo Systems, Denmark) using 75 ml min^{-1} air as the mobile phase with the temperature of the injector set equal to the ambient temperature. The N_2O concentration was analysed by means of gas chromatography (Shimadzu Co., Japan) equipped with an electron capture detector (ECD) and a Porapak column Q 80–100 mesh 2 m*2 mm retention gap, using 22 ml min^{-1}. N_2 was the carrier gas, and the injector, column, and detector temperatures were 80, 70, and 320 °C, respectively.

E. Data Analysis

Statistical analyses were done with SPSS® software (v. 17.0 for Windows). The Kolmogorov-Smirnov test was used to check the normality of the data. This normality check was done to determine whether parametric or non-parametric tests should be applied to analyse the data. To determine the differences in GHG fluxes from the different sample points, the Kruskal-Wallis and Mann Whitney non-parametric tests ($\alpha = 0.05$) were used. In addition, the relationship among the environmental data and GHG fluxes was estimated by using Spearman correlation coefficients.

III. Results and Discussion

A. Water Characteristics

TABLE I
WATER CHARACTERISTICS OF THE SONSO LAGOON (MEAN AND STANDARD DEVIATION ARE SHOWN)

Parameter	Sampling Point			
	P1	P2	P3	P4
Depth (m)	0.6±0.3	0.5±0.5	0.7±0.5	0.6±0.6
Water temperature (°C)	26.8±2.5	28.7±2.9	30.3±2.8	30.4±2.6
Water transparency (m)	0.1±0.1	0.1±0.1	0.1±0.1	0.2±0.1
pH (units)	7.8±0.5	7.8±0.4	7.9±0.4	7.8±0.5
Alkalinity (mg $CaCO_3.l^{-1}$)	172.8±52.2	215.7±55	227.2±37	256.2±40
DO (mg. l^{-1})	4.4±2.2	4.5±1.7	5.4±1.6	4.6±1.6
COD (mg $O_2.l^{-1}$)	33.8±9.5	31.6±12	31.7±12.3	32.1±12.2
TN (mg.l^{-1})	1.3±1.1	1.2±1.4	1.8±2.1	1.7±1.8
NH_4^+-N (mg.l^{-1})	1.0±0.5	0.9±0.6	0.7±0.4	0.5±0.3
NO_3^--N (mg.l^{-1})	0.06±0.08	0.08±0.1	0.07±0.09	0.12±0.1
TP (mg .l^{-1})	0.17±0.11	0.31±0.15	0.24±0.08	0.08±0.1
PO_4^{-3}- P (mg.l^{-1})	0.07±0.04	0.16±0.09	0.11±0.07	0.05±0.1

In Table I are shown the concentrations of dissolved oxygen (DO), total phosphorus (TP), and total nitrogen (TN) measured in the Sonso Lagoon. The DO concentrations

measured indicate that in the SL there was oxygen depletion for all the sampling points, thus OD values such as 4.4 mg.l^{-1} were measured. The TN ranged from1.2 to 1.8 mg.l^{-1} while TP varied between 0.05 and 0.08 mg.l^{-1}indicating nutrient excess. Also the transparency was lower than reported for non-eutrophic aquatic ecosystems. Further, COD ranged from 20 to 40 mg O_2.l^{-1}, which is above the values in water quality guides for freshwater (20 mg O_2.l^{-1}) [19].

The water characteristics measurements indicated that the Sonso Lagoon is eutrophic. This can be explained due to the input of organic matter and nutrients from the River Cauca, agricultural run-off, and domestic sewage discharges.

B. GHG Fluxes

Methane

The median methane fluxes for P1, P2, P3 and P4 were 0.037, 0.116, 0.078, and 0.059 g.m^{-2}.d^{-1}, respectively (Fig. 2). In general, P1, P2, P3 and P4 were net sources of methane. The only significant difference in flux was observed between P1 and P4 (p = 0.012).

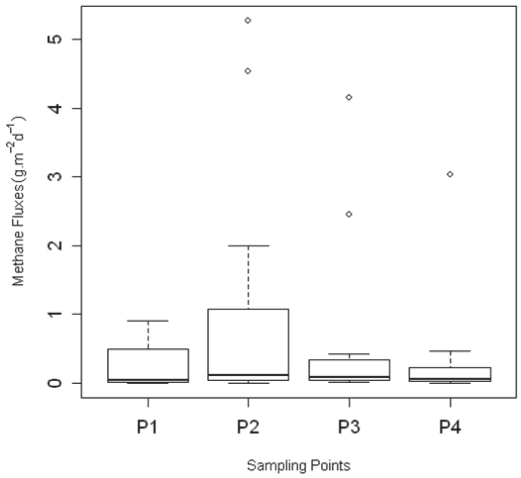

Fig. 2 Flux of CH_4 in the Sonso Lagoon

TABLE II
SPEARMAN CORRELATIONS BETWEEN CH_4 FLUXES AND WATER CHARACTERISTICS

Parameter	P1	P2	P3	P4
DO	n.o	(0.048;-50%)	n.o	n.o
COD	(0.03;55%)	(0.03;62%)	n.o.	n.o.
PO_4^{-3}- P	(0.04;66%)	n.o	(0.112;57%)	n.o
NO_3^--N	n.o	(0.044;59%)	(0.12;78%)	(0.45;-68%)
NH_4^+-N	n.o	(0.01;77%)	n.o	n.o
pH	n.o	(0.001;-75%)	n.o	n.o

n.o. = Spearman correlation was not observed

In Table II can be observed the correlations of Spearman between CH_4 fluxes and water characteristics at the four points. No correlation could be identified between methane flux and the water temperature or the ORP (p>0.05). Positive correlations (p<0.05) were found between methane flux, $PO4^{-3}$ and COD at P1. By contrast, in P2, DO and pH showed negative correlation whereas COD, NO_3^-N, NH_4^+-N, were correlated positively to the CH_4 emissions. Although in P3 and P4 there were correlations between methane fluxes and $PO4^{-3}$ (r = 0.57; p = 0.112), and NO_3-N (r = -.68; p = 0.45), it was not significant (p>0.05).

Carbon Dioxide

The CO_2 fluxes for P1, P2, P3, and P4 were 0.9, 0.8, 2.8 and -3.48 g CO_2.m^{-2}.d^{-1}, respectively (Fig. 3). The statistic comparison between the four points indicated that P4 showed significant differences among P1, P2, and P3 (P1: p = 0.0002; P2: p = 0.0001; P3: p = 0.0001; Mann Witney test). P4 seems to be a CO_2 sink contributing to carbon sequestration in the FW.

In Table III are shown the correlations of Spearman between CO_2 fluxes and water characteristics at the four points. COD, TP, NO_3^--N, and NH_4^+-N were the most important parameters influencing the CO_2 fluxes from the Sonso Lagoon. At P1, CO_2 fluxes were positively correlated to COD and negatively correlated to NH_4^+-N (p<0.05). In P2, the concentration measures of TP and NO_3^--N (r = 0.89; p = 0.06) showed a positive correlation with CO_2 fluxes (p>0.05). In P2 a negative correlation between NH_4^+-N and CO_2 release (r = -.55; p = 0.04) was also observed. P3 showed no significant correlation between CO_2 fluxes and the environmental parameters. In P4, the CO_2 fluxes were negatively correlated to the alkalinity (r = -.71; p = 0.05).

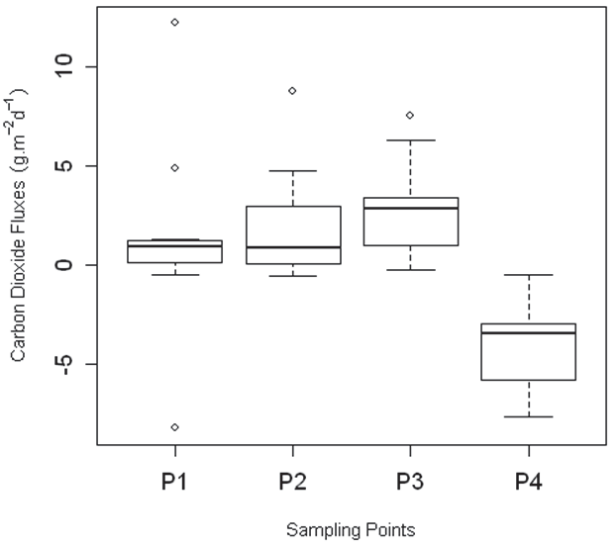

Fig. 3 Flux of CO_2 in the Sonso Lagoon

A wide range of GHG emissions are reported in the literature. The mean emissions of CO_2 fluxes in this study were higher than observed in other natural systems [20], [21], [11], [15] but are comparable to values from constructed wetlands treating municipal wastewater [13], [22]. On the other hand, the methane emissions from the Sonso Lagoon were mostly higher than observed in other FWs [20], [21], [11], [15] and comparable to some eco-technological systems for wastewater treatment [13], [22]-[24].

TABLE III
SPEARMAN CORRELATIONS BETWEEN CO_2 FLUXES AND WATER CHARACTERISTICS

Parameter	P1	P2	P3	P4
COD	(0.07; 57%)	n.o.	n.o.	n.o.
TP	n.o.	(0.001; 58%)	n.o.	n.o
NO_3^--N	n.o	(0.06; 89%)	n.o.	n.o
NH_4^+-N	(0.04;-62%)	(0.04;-55%)	n.o	n.o

n.o. = Spearman correlation was not observed

The results obtained suggest that in general, the Sonso Lagoon was a CH_4 and CO_2 net source. This could be attributed to the eutrophication that suffers this lagoon. In the case of non-anthropogenic intervention, most FWs are net carbon sinks because primary production is often able to sequester more carbon at greater rates than respiration-accreting organic matter into soils over time [25]. However, in natural wetlands that receive wastewater i.e. the Sonso Lagoon, this ability to sequester carbon is affected because the nutrient and organic matter loading enhances mineralization and thus the CH_4 and CO_2 emissions [25], [10], [13], [7], [4].

The variability of CO_2 and CH_4 fluxes in the Sonso Lagoon could not be explained by temperature water changes. This is because all the data were collected during daytime to maximum higher solar radiation and no changes in the water temperature were observed for the different monitoring campaigns.

In this study, the fluxes of CH_4 correlated negatively with both pH and DO and positively with COD at point P2. The organic matter (COD) in P2 enters from sewage and agricultural run-off discharges increasing the oxygen demand. This condition favours anaerobic decomposition in the sediments producing CH_4 that can be released into the atmosphere. In other words more external organic matter and less available oxygen increase CH_4 emissions. The negative correlation between pH and CH_4 fluxes can be explained by the optimum conditions in which the methanogenesis process is carried out, which is between 6.0 and 7.0. In this study, the pH values were higher than 7.0, and thus these conditions indicate that CH_4 production was influenced by this factor.

The presence of PO_4^{-3} and NH_4^+-N was positively correlated to CH_4 fluxes while apparently NO_3-N decreased CH_4 fluxes. PO_4^{-3} stimulated CH_4 emissions from the Sonso Lagoon, as was reported for lakes and ditches from The Netherlands and Sweden [23], [15]. This is because the increment of PO_4^{-3} in lakes under eutrophication stimulates the transformation of organic matter to methane [10], [26]-[28]. In the same way, the results indicate that an increase in NH_4^+-N increased CH_4 fluxes from the Sonso Lagoon. This increase can be explained because elevated NH_4^+-N concentration inhibits CH_4 oxidation [29], [30]. This inhibition is attributed to competition between NH_4^+-N and CH_4 for binding sites on methane monooxygenase, because of their similar chemical structure [31]. Also the negative correlation between NO_3^- -N and methane production found in this study has been reported in previous studies [23], [32]. Under anaerobic conditions the organic matter is used by methanogens to produce methane, but at higher NO_3^--N concentrations denitrification is favoured above methanogenesis [12].

Carbon dioxide emissions from the majority of the points in the Sonso Lagoon (P1, P2, P3) were correlated to the NO_3^--N, NH_4^+-N, and TP concentrations. The presence of these nutrients introduces shifts in decomposition rates and nutrient cycling mainly when wetlands become eutrophic. The positive correlation of NH_4^+-N with CO_2 emission is in line with the findings of wetlands in The Netherlands [15]. Nitrates serve the first terminal electron acceptor in wetland soils after oxygen depletion, making them an important chemical in the oxidation of organic matter in wetlands [33]. Denitrifying bacteria play an important role in the carbon cycle of wetlands as they contribute significantly to the carbon mineralization budget (up to 50%) of the carbon mineralized in eutrophic freshwaters [34]. The positive correlation between TP and CO_2 emissions can be explained by the fact that bacteria depend on phosphorous as a nutrient in the microbial organic matter decomposition [35].

The water characteristics at P1, P2 and P3 were similar, what could be the reason why no significant spatial variations in CH_4 and CO_2 fluxes were observed in the Sonso Lagoon. Only sampling point P4 was significantly different with respect to the CH_4 and CO_2 fluxes. This can be explained because P4 by contrast to P1, P2 and P3 was dominated by floating vegetation such as *Eichhornia crassipes, Salvinia* sp., and *Pistia stratiotes* that probably regulated the CH_4 and CO_2 emissions: (i) acting as a physical barrier to prevent the methane diffusion across the water interface into the atmosphere [36], [24], [37]; (ii) sequestering CO_2 by algae and floating plant photosynthesis [25], [38], [22]; and (iii) favouring methane oxidation through translocation of oxygen gaseous produced by photosynthetic activity of the green leaves to the stems and roots and to the water body [39].

The methane fluxes from floating vegetation measured in the Sonso Lagoon (P4) were lower than those reported for emergent macrophytes in other natural wetlands. This suggests that floating plants i.e. *Salvinia sp* have a lower capability to transport CH_4 compared with emergent macrophytes i.e. *Phragmites australis*. This methane-releasing capacity in emergent macrophytes has to do with their continuous access to the atmosphere and their high potential to exchange gases primarily by internal pressurization and convective gas flows [39]-[41]. The superiority of emergent macrophytes compared with floating vegetation with respect to methane emissions was observed in an arid lake area in western China [42] and a southern boreal lake [43]. Likewise, [44] showed that macrophytes, rather than phytoplankton, directly positively affected CH_4. These results and the findings of the current study indicate that species type and areal coverage of the dominating species should be carefully considered when estimating the emissions of CH_4 from wetlands.

Nitrous Oxide

The median N_2O fluxes for P1, P2, P3, and P4 were 0.01, 0.25, 0.19 and -3.19 mg N_2O m^{-2} d^{-1}, respectively (Fig. 4). The negative median fluxes in P4 indicate that this point acts as a

N_2O sink. At the other points N_2O was emitted. Only P4 showed significant differences compared to P1, P2, and P3.

The N_2O fluxes in the Sonso Lagoon were mostly higher than observed in boreal ponds and FWs [20], [21], [45], [46] and matched with constructed wetlands that receive sewage [47], [13], [32], [22]. The negative fluxes observed in the Sonso Lagoon were also reported for free water surface constructed wetlands [47], [13], [22].

As can be seen in Table IV, the N_2O emissions from P2 were positively correlated to TN and NO_3^-N. By contrast, in P1, P3, and P4 there were not correlations between N_2O fluxes and the environmental parameters measured.

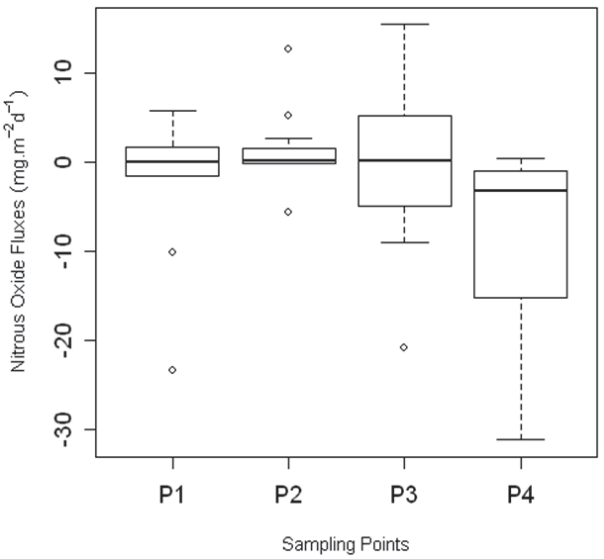

Fig. 4 Flux of N_2O in the Sonso Lagoon

Total nitrogen and NO_3^- influenced the production of N_2O at P1 and P2. This can be explained because N_2O is an intermediate of nitrification and denitrification and its atmospheric release depends on the availability of N (NO_3^-, NO_2^-, or NH_4^+) and oxygen [48], [49]. The presence of N-NO_3, N-NO_2, or N-NH_4^+ is related to wastewater discharges, sediment exchange from the Cauca River, and agricultural run-off. Nitrifying bacteria may produce NO and N_2O either as a side-product in the catabolic pathway (oxidizing ammonia to nitrite), or, alternatively, denitrifying bacteria may produce NO or N_2O converting nitrite with ammonia, hydrogen or pyruvate as an electron donor [50]-[52].

TABLE IV
SPEARMAN CORRELATIONS BETWEEN N_2O FLUXES AND WATER CHARACTERISTICS

Parameter	P1	P2	P3	P4
TN	n.o	(0.026;69%)	n.o.	n.o.
NO_3^--N	n.o	(0.09; 60%)	n.o.	n.o

n.o. = Spearman correlation was not observed

Nitrous oxide dynamics in wetland plants has been previously described [47], [53], [13], [22]. In the zones with vegetation, N_2O is both emitted and sequestered depending on the type of vegetation. The presence of vascular plants affects the gas fluxes and leads to significantly higher emissions from most of the vegetated zones [22]. The aerenchymal tissue is more active in the transport of gases from the soil to the atmosphere in vascular plants than in floating plants.

In the current study, it was found that N_2O was taken up in the zone dominated by floating plants and algae and the transport of this gas into the atmosphere was probably limited. This result is in line with the observations in a constructed wetland treating wastewater [54]. The N_2O consumption has also been attributed to NO_3^- concentration lower than 0.5 $mg.l^{-1}$ [54]. This shortage of electron acceptor produces N_2O consumption by denitrifying bacteria. In the Sonso Lagoon, the measurements indicated that NO_3^- was around 0.10 $mg.l^{-1}$ and therefore the emissions of this gas into this atmosphere were decreased. However, it is necessary to elucidate the exact mechanism that affects this N_2O consumption and its relation to other environmental factors and vegetation.

IV. CONCLUSION

The current study focused on GHG emissions from a eutrophic tropical FW located in Colombia. According to the measurements carried out during one year it was possible to conclude that this FW was a net source of CO_2, CH_4, and N_2O. This indicates the impact of anthropogenic activities such as agricultural run-off and wastewater discharges on wetlands switching their ability to sequester C and N to sources of GHGs. Thus, increasing the nutrient loads and input of organic substrates will probably enhance the contribution to global warming of FWs.

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