Original Research

# Methane Emission in Mangrove Forests: Field Study and Environmental Correlations from Xuan Thuy National Park, Vietnam

Hanh Thi Minh Pham<sup>1</sup>, Ba The Dang<sup>2</sup>, Cuong Tu Ho<sup>3</sup>, Nghi Thanh Duong<sup>4</sup>, Hanh Thi Nguyen<sup>5</sup>, Quynh Thi Phuong Le<sup>6</sup>, Thuy Thi Duong<sup>3</sup>, Ha Manh Bui<sup>7\*</sup>

<sup>1</sup> Institute of Mechanics (IMECH), Vietnam Academy of Science and Technology (VAST), 264 Doi Can, Ba Dinh, Hanoi 10000, Vietnam

<sup>2</sup> University of Engineering and Technology (UET), Vietnam National University (VNU), 144 Xuan Thuy, Cau Giay, Hanoi 10000, Vietnam

<sup>3</sup> Institute of Environmental Technology (IET), Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Cau Giay, Hanoi 10000, Vietnam

<sup>4</sup> Institute of Marine Environment and Resources (IMER), Vietnam Academy of Science and Technology (VAST), 246 Da Nang, Ngo Quyen, Hai Phong 04000, Vietnam

<sup>5</sup> Institute of Chemistry (ICH), Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Cau Giay, Hanoi 10000, Vietnam

<sup>6</sup> Laboratory of Environmental Chemistry, Institute of Natural Products Chemistry, Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Cau Giay, Hanoi 10000, Vietnam

<sup>7</sup> Faculty of Environment, Saigon University, 273 An Duong Vuong Street, District 5, Ho Chi Minh City 70000, Vietnam

Received: 12 November 2023 Accepted: 25 January 2024

# **Abstract:**

This study investigates methane emissions in the mangrove forests of Xuan Thuy National Park in Vietnam, examining seasonal variations and the influence of environmental factors. Data from the field measurements present methane flux rates ranging from 0.01 to 10.42 mg m<sup>-2</sup> day<sup>-1</sup>, are substantially lower than the default estimations recommended by IPCC guidelines. The study highlights discrepancies between actual field measurements and suggested default values, emphasizing the necessity for site-specific monitoring to avoid overestimating greenhouse gas emissions, particularly in mangrove areas. The analysis reveals strong correlations between methane flux and environmental parameters. Factors such as water pH, turbidity, temperature, and nitrogen content significantly influence methane emissions. The study emphasizes the interconnectedness of various greenhouse gas emissions within mangrove ecosystems and underlines the importance of accurate, location-specific data in environmental assessments and policy-making.

Keywords: Xuan Thuy national park, environmental factors, mangrove, methane emission, Vietnam.

# Introduction

Greenhouse gases, including carbon dioxide  $(CO_2)$ , methane  $(CH_4)$ , nitrous oxide (N2O), and fluorinated gases (F-gases), are released into the atmosphere due to various human activities on a global scale. Methane,

\* e-mail: manhhakg@sgu.edu.vn

ranking as the second most prevalent greenhouse gas after carbon dioxide, contributes approximately 16% to the total global greenhouse gas emissions [1]. While human-related sources like agriculture, waste management, energy consumption, and biomass burning are recognized as major contributors to  $CH_4$  emissions, recent scientific investigations have highlighted natural emission occurrences from mangrove forests [2-4].

Mangrove ecosystems span approximately 14.8 million hectares globally, with Indonesia (19%), Brazil (9%), Nigeria (7%), and Mexico (6%) accounting for a substantial 40% of this total area [5]. In Vietnam, these vital ecosystems cover roughly 164701 hectares, predominantly distributed across the North (28%) and the South (70%), with the Xuan Thuy mangrove forest serving as a significant representation in the Northern region [5]. Traditionally acknowledged as crucial "blue carbon" ecosystems alongside seagrass beds and salt marshes, concerns have arisen regarding the potential impact of greenhouse gas emissions, particularly methane, on the carbon storage capacity of mangrove ecosystems [3, 6]. Processes such as fermentation and decomposition within the mud of mangrove forests have been identified as sources of gases such as H<sub>2</sub>S, N<sub>2</sub>O, and notably CH<sub>4</sub>. Acknowledging the significance of mangrove forests as reservoirs of carbon, Vietnam has undertaken studies assessing carbon stocks in various mangrove areas. These include studies in the Can Gio mangrove forest park in Hochiminh City and investigations of carbon stocks in Kandelia obovata and Sonneratia caseolaris forests in Kim Son, Ninh Binh province [3, 7, 8].

Vietnam has actively engaged in global climate change initiatives and, post-COP26, has committed to significant goals for greenhouse gas emissions reduction. These commitments involve aiming for carbon neutrality by 2050 and targeting a 30% reduction in methane emissions by 2030, specifically focusing on key sectors like energy, waste, agriculture, forestry, and land use (AFOLU) [1]. Consequently, conducting comprehensive greenhouse gas emissions inventories, particularly regarding methane emissions, becomes imperative to strategize and implement effective reduction plans.

However, research specifically addressing methane emissions from wetland ecosystems, especially mangrove forests in Vietnam, remains limited. Therefore, this study aims to estimate CH<sub>4</sub> emissions and explore the relationship between factors such as mangrove age, environmental conditions, and methane emission levels within the Xuan Thuy mangrove forests. These findings will not only contribute valuable insights to greenhouse gas inventory practices but will also inform crucial environmental management strategies tailored for wetland ecosystems, particularly mangrove forests. Furthermore, the outcomes of this study will provide essential data necessary for establishing Tier 2 - countryspecific Emission Factors (EF) for Vietnam.

## **Study Area and Methods**

#### The Study Area

Xuan Thuy National Park, Nam Dinh Province, was the first wetland in Southeast Asia to join the RAMSAR International Convention (The Convention on Wetlands of International Importance especially as Water- fowl Habitat) in January 1989. In January 2003, Xuan Thuy wetland nature reserve became Xuan Thuy National Park, and in December 2004, Xuan Thuy National Park was recognized by UNESCO as the core area of the World Biological Reserve in the inter-provincial coastal area of the Red River Delta. 95% of mangrove vegetation in the Xuan Thuy National Park is *Kandelia obovataa*, and the remaining is *Sonneratia caseolaris* (L.) Engl. and *Rhizophora stylosa* [9].

In Nam Dinh province, the climate divides into the rainy season (from May to October) and the dry season (from November to the next April). During 2013-2022, in April and August, the monthly average air temperature varied from 22.0 to 26.7 °C (mean value:  $24.5 \pm 1.2^{\circ}$ C) and from 28.5 to  $31.1^{\circ}$ C (29.1  $\pm$  0.5°C), respectively. Meanwhile, monthly rainfall at Nam Dinh station ranged from 18.6 to 148.8 mm (97.2  $\pm$  47.5 mm) in April and from 148.2 to 515.0 mm (354 $\pm$ 107.5mm) in August (data not shown).

## **Materials and Methods**

## Sample Collection and Site Description

The study encompassed three distinct areas: old stand mangrove areas (abbreviated as RG) (>17 years old), young stand mangrove areas (RTS) (<11 years old) and a non-forest control area (BL). Within each area, sampling occurred at three sites, each maintaining a submerged depth of approximately 40-50cm, spaced roughly 20m apart (refer to Fig. 1). Soil, water, and methane samples were gathered from these sites. The fieldwork was conducted on April 11-12 (dry season) and August 13-14 (rainy season) 2019, specifically during low tide and daytime between 10 am - 4 pm local time.

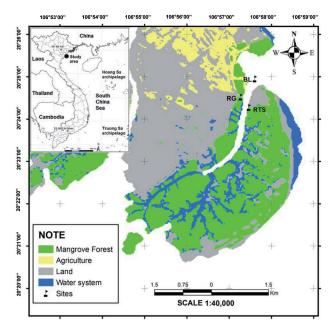


Fig. 1. Sampling areas (BL: non-forest control area), (RG: old stand mangrove areas), and (RTS: young stand mangrove areas)

### Water and Soil Sampling

At each site, three random sediment cores measuring 30 x 30 cm<sup>2</sup> were collected and thoroughly mixed. A total of fifty-four soil samples were obtained at three different depths (0-5 cm, 15-20 cm, and 35-40 cm) using a polyvinyl chloride (PVC) core. All samples were immediately stored in a cool box for subsequent laboratory analysis, which included Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, Total Phosphorus (TP), and Total Nitrogen (TN).

Eighteen water samples were collected approximately 5-10cm below the water surface. Sample containers were rinsed three times with the respective water samples. Preservation of samples for TN, TP, NO<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> analysis was carried out following the Standard Methods for the Examination of Water and Wastewater [10].

#### In-Situ Water Quality Measurement

In-situ water quality parameters, including water temperature (Tw), pH, Dissolved Oxygen (DO), turbidity, and salinity (sal), were measured in triplicate using the TOA model WQC-22A water quality checker.

Dissolved nutrients (PO43-, NO3-, and NH4+) were analyzed spectrophotometrically using a UVspectrophotometer (DR6000, HACH, USA), VIS following specific methods such as the Ultraviolet Spectrophotometric Screening Method (APHA method 4500-NO<sub>3</sub>-B) for NO<sub>3</sub>-, the Ascorbic Acid Method (PO<sub>4</sub>: 4500-P E) for orthophosphate quantification, and the Salicylate Method proposed by Reardon et al. in 1966 for NH<sub>4</sub><sup>+</sup> concentration determination [10, 11]. Total phosphorus (TP) was measured according to ISO 6878: 2004, employing the Ammonium Molybdate spectrometric method, while total nitrogen (TN) was quantified referring to ISO10048: 1991, utilizing Catalytic Digestion after reduction with Devarda's alloy. Each measurement was performed three times, and the reported value represents the average of these three measurements (confidence > 90%).

## Collection and Measurement of Methane Samples

Methane emissions were quantified using a widely adopted floating chamber system method [12]. The system comprised a custom-made cylindrical polyvinyl chloride (PVC) dark chamber (volume: 0.01292 m<sup>3</sup>; water-air interface: 0.06154 m<sup>2</sup>; height: 21 cm) equipped with a thermometer and an internal fan. Gas samples were manually extracted from the chamber four times at 0, 10, 20, and 30-minute intervals using separate syringes. These samples were immediately stored in pre-evacuated 12 ml glass vials (15.5mm diameter, Labco Limited, UK) for subsequent analysis via gas chromatography-flame ionization detection (GC-FID). The flame ionization detector was set at 300°C, maintaining the oven temperature at 50°C, with helium (99.99%) utilized as the carrier gas for methane concentration measurement.

## Methane Flux Rate Calculation

The methane flux rate (F in  $mg/m^2/day$ ) at the time of chamber closure was determined using Equation 1 proposed by Smith and Conen [13].

$$F = \frac{\Delta C}{\Delta t} \times \frac{\nu}{A} \times \frac{M}{V} \times \frac{P}{P_0} \times \frac{273}{T}$$
(1)

Where:  $\Delta C/\Delta t$  is the change in concentration in time interval; v and A are the chamber volume and area; M is the molecular weight of methane (16.04g/mole); V is the volume occupied by 1 mole of gas at STP (0.024m<sup>3</sup> or 22.4 L); P is the barometric pressure (mbar); P<sub>0</sub> is the standard pressure (1103 mbar); T is the ambient temperature (K). v/A may be substituted by the average chamber height. In areas close to sea level, the pressure factor can often be disregarded.

# Methane Emission Factors (EFs) by the Intergovernmental Panel on Climate Change (IPCC)

Addressing the global climate change challenge necessitates accurate national greenhouse gas inventories. In 2006, the IPCC introduced the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Furthermore, the 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Wetlands (Wetlands Supplement) was issued in 2013. According to this guideline, methane emission factors (EFs) are categorized into default data or Tier 1; country-specific data, known as Tier 2; and values derived from the most detailed methods, such as modeling, designated as Tier 3. The Tier 1 approach using default data serves as the primary reference in regions lacking Tier 2 and 3 EFs [6]. For mangrove CH4 emission, the default EF was identified as 193.7 kg CH<sub>4</sub> ha<sup>-1</sup> y<sup>-1</sup> for tidal freshwater and brackish marshes and mangroves exhibiting salinity < 18ppt. Areas with salinity >18ppt were designated as 0 kg  $CH_4$  ha<sup>-1</sup> y<sup>-1</sup> for methane emissions [14].

## Statistical Analysis

We assessed seasonal (rainy vs. dry) and spatial (mangrove area vs. non-forest control area) differences in various variables (pH, DO, water temperature, turbidity,  $NH_4^+$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , TN, TP) in water samples and airwater methane flux using the non-parametric Mann-Whitney U test. Significance was determined at p < 0.05. Additionally, Spearman's rho test examined correlations between methane fluxes and different water and soil quality variables. Statistical analyses were conducted using SPSS 20.0 software for Windows.

#### **Results and Discussion**

Water and Sediment Physical-Chemical Characteristics

Surface water temperature in the mangrove area (RG and RTS) ranged from 26.0 to 31.9°C (average 29.3±2.5°C); DO: 5.3 - 8.0 mg/L (6.4±1.3mg/L);

pH: 7.1 - 8.1 (7.6 $\pm$ 1.2). In the non-forest control area (BL), temperature ranged from 27.8 to 33.5°C (31.1 $\pm$ 2.9°C); DO: 4.2 - 6.7mg/L (5.4 $\pm$ 1.0mg/L); pH: 7.3 - 7.8 (7.6 $\pm$ 0.2). All DO and pH measurements met Vietnam's National Technical Regulation on Marine Water for Aquatic Life Protection (QCVN 10: 2023/BTNMT).

The mangrove area showcased a diverse range of nutrient concentrations:  $NO_3^-$  spanned from 0.33 to 0.46 mg/L (average 0.41±0.12 mg/L), while  $NH_4^+$  ranged from 0.17 to 0.36mg/L (0.25±0.09 mg/L), and  $PO_4^{3-}$  from 0.01 to 0.06 mg/L (0.03±0.02 mg/L). TN ranged from 3.0 to 12.4mg/L (6.7±3.68 mg/L), and TP from 0.15 to 0.28mg/L (0.21±0.07 mg/L). Notably, ammonium concentrations exceeded permissible values, while phosphate levels were below regulatory limits. These findings underscore the substantial variance in nutrient content within the mangrove area, indicating a significant accumulation of nitrogen and phosphorus compared to nearby coastal regions. A comparative analysis conducted by Le et al. [15] on nutrient concentrations (in mg/L) from 36

samples of aquaculture coastal seawater in the Tien Hai district during 2019-2020 revealed:  $NO_3^{-}N$ : 0.05 to 1.22 (mean 0.37);  $NH_4^{+}$ -N: 0.02 to 0.39 (mean 0.13);  $PO_4^{3^{-}}$ -P: 0.01 to 0.09 (mean 0.03); TN: 0.79 to 1.86 (mean 1.08); TP: 0.03 to 0.28 (mean 0.12). These findings indicate significantly higher nutrient concentrations, particularly in TN and TP, within the mangrove forest area compared to the neighboring Tien Hai and Thai Binh coastal areas, which represent the adjacent estuary. This observation corroborates similar findings from various global studies, including those conducted at Dongzhai Port, China [16]; Yunxiao National Mangrove Reserve and Zhangjiang Estuary, Southeast China [17]; and San Juan Bay Estuary, Puerto Rico, United States [18].

Higher water temperatures were observed in the BL area compared to mangrove areas (p<0.05). Conversely, DO concentration (p<0.05), turbidity (p<0.01), and nutrients ( $NO_3^{-1}$  and  $PO_4^{-3-}$ ) were lower in the BL area. No distinct spatial variations were noted for other monitored parameters (Table 1). Comparing water quality between

Doromotor	Concentration min-max (mean ± SD)				
Parameter	Mangrove area	Non-forest control area			
Tw (°C)	26.0-31.9 (29.3±2.5)	27.8 - 33.5 (31.1±2.9)*			
DO (mg/L)	5.3-8.0 (6.4±1.3)	4.2-6.7 (5.4±1.0)*			
pН	7.1-8.1 (7.6±1.2)	7.3 - 7.8 (7.6±0.2) 0.5-1.0 (0.7±0.2)			
Salinity %	0.2-1.7 (0.8±0.5)				
Turbidity (NTU)	25-311 (111±75)	26-46 (36±7)**			
NO <sub>3</sub> <sup>-</sup> -N (mg/L)	0.33-0.46 (0.41±0.04)	0.27-0.40 (0.34±0.05)*			
$PO_4^{-3}-P(mg/L)$	0.01-0.06 (0.028±0.017)	0.01-0.02 (0.018±0.004)			
NH4+-N (mg/L)	0.17-0.36 (0.25±0.06)	0.21-0.25 (0.23±0.01)			
T-N (mg/L)	3.0-12.4 (6.7±3.6)	3.1-10.7 (6.1±3.6)			
T-P (mg/L)	0.15-0.28 (0.21±0.04)	0.08-0.18 (0.13±0.04)*			

Table 1. Water quality in mangrove forest and non-forest control area.

Note: \*: significant difference between mangrove and non-forest areas (p<0.05); \*\* significant difference between mangrove and non-forest areas (p<0.01);SD: standard deviation

Table 2. Seasonal variable in water quality, Xuan Thuy mangrove areas.

Parameters	Concentration min-max (mean ± SD)					
Parameters	Dry season	Rainy season				
Tw (°C)	26.0-27.0 (26.6±0.4)	31.0-31.9 (31.5±0.3)**				
DO (mg/L)	6.03-8.04 (7.05±0.59)	5.30-6.45 (5.85±0.35)**				
pH	7.82-8.07 (7.94±0.08)	7.05-7.77 (7.39±0.14)**				
Salinity %	0.45-1.68 (1.14±0.53)	0.15-0.88 (0.45±0.29)**				
Turbidity (NTU)	79-311 (157±78)	25-215 (74±44)**				
NO <sub>3</sub> <sup>-</sup> -N (mg/L)	0.40-0.46 (0.43±0.02)	0.33-0.45 (0.39±0.04)				
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	0.25-0.36 (0.30±0.04)	0.17-0.26 (0.21±0.04)				
T-N (mg/L)	3.0-4.1 (3.5±0.4)	6.6-12.4 (9.92±2.07)*				
PO <sub>4</sub> - <sup>3</sup> -P (mg/L)	0.01-0.06 (0.03±0.02)	0.01-0.04 (0.02±0.01)				
T-P (mg/L)	0.17-0.26 (0.21±0.03)	0.15-0.28 (0.21±0.05)				

*Note:* \*: significant difference between the two seasons (p < 0.05); \*\* significant difference between the two seasons (p < 0.01); SD: standard deviation

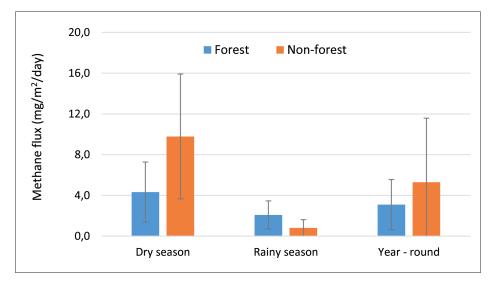


Fig. 2. Mean values of methane flux in the forest and non-forest controlled areas

old and young mangrove areas, lower temperatures were observed in RG, while  $NO_3^{-1}$  and  $PO_4^{-3-1}$  concentrations were higher (p<0.05). Other parameters showed no statistically significant differences between these two forest areas (Table 2).

Seasonally, in mangrove areas, average water temperature (p<0.01) and TN concentration (p<0.05) were lower during the dry season than in the rainy season, whereas DO, pH, salinity and turbidity were higher in the dry season than the rainy one (p<0.05). Higher TN concentration in the rainy season implied the sampling sites received input from terrestrial sources through the river. Since the sites were located inside the mangrove, which were not directly impacted by the river flow and current, so lower salinity, and turbidity in the study area were detected because of the dilution effect during the rainy season.

The sedimentary environment quality of the research area was reported in the previous study [9]. The mangrove forest areas were different from the non-forest control area by the accumulation of C, N, and P components in the sediment. The old-stand forest stored more C and N in its sediment than the young-stand forest, which had less P component. The influence of hydraulic dynamics in the non-forest control area (BL area) leads to a mixture and no stratification in the soil sample collected in this area.

Table 3. CH<sub>4</sub> emissions in mangrove forests and non-forest control areas.

	Methane emission (mg $m^{-2} day^{-1}$ )						
Area	Dry season season min-max (mean ± SD)	Rainy season min-max (mean $\pm$ SD)					
RG	0.89-10.42 (4.69±2.89)	1.15-5.05 (2.97±1.37)					
RTS	0.20-9.13 (3.65±3.16)	0.01-2.74 (1.43±1.10)*					
BL	5.26-16.76 (9.79±6.13)	0.04-1.64 (0.81±0.80)**					

*Note:* \*: significant difference between the two seasons (p<0.05); \*\* significant difference between the two seasons (p<0.01); SD: standard deviation; RG: old – stand forest; RTS: young – stand forest; BL: non – forest controlled area

# CH<sub>4</sub> Fluxes

As seen in Fig. 2, throughout both seasons, methane (CH<sub>4</sub>) fluxes within the mangrove forest and non-forest control areas ranged from 0.01 to 10.42 (mean value:  $3.09 \pm 2.47$ ) and 0.04 to 16.76 ( $5.30 \pm 6.28$ ) mg m<sup>-2</sup> day<sup>-1</sup> (equivalent to 0.001-0.649, 0.193\pm0.154, and 0.002-1.044, 0.330\pm0.391 m mole m<sup>-2</sup> day<sup>-1</sup>), respectively. No significant differences were observed in CH<sub>4</sub> fluxes between these two areas (p > 0.05). Similarly, during the rainy season, average CH<sub>4</sub> emissions were 2.08±1.39 mg m<sup>-2</sup> day<sup>-1</sup> in the control area, also lacking significant differences (p>0.05). However, in the dry season, emissions from the forest area (4.33±2.95 mg m<sup>-2</sup> day<sup>-1</sup>) were lower compared to the control area (9.79±6.13 mg m<sup>-2</sup> day<sup>-1</sup>) (p<0.05).

Notably, the average CH<sub>4</sub> flux in the RG area was significantly higher (p<0.05) than that in the RTS area (3.81±2.42 mg m-2 day-1 and 2.33±2.36 mg m<sup>-2</sup> day<sup>-1</sup>, respectively) over the two seasons. This trend persisted in the rainy season (RG: 2.81±1.76 mg m<sup>-2</sup> day<sup>-1</sup>; RTS: 1.43±1.14 mg m<sup>-2</sup> day<sup>-1</sup>) (p<0.05) but not in the dry season (RG: 4.81±3.31 mg m<sup>-2</sup> day<sup>-1</sup>; RTS: 3.68±2.87 mg m<sup>-2</sup> day<sup>-1</sup>) (p>0.05). This discrepancy may result from higher organic carbon accumulation in the RG as opposed to the RTS [9].

Seasonal variation analysis displayed consistent methane emissions in the old-stand forest area and a distinct increase in emissions during the dry season compared to the rainy season in the RTS and BL areas, as seen in Table 3.

The estimated methane flux in the Xuan Thuy mangrove area at 0.04 to 38.03 (11.28±9.02) kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup>, significantly lower than the IPCC's default EF of 193.7 kg kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup>. Caution is advised during kg CH<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup> greenhouse gas inventory in mangrove areas to avoid overestimation, necessitating further research on methane emissions in wetlands and mangrove forests for more accurate country-specific values.

Moreover, Ha's study [19]on carbon stock and flux in planted mangroves at Xuan Thuy National Park reported an average water-air carbon emission by CO<sub>2</sub> gas of 1.15 MgC ha<sup>-1</sup> year<sup>-1</sup>. These findings indicate additional carbon emissions due to methane emission, averaging  $3.09 \pm 2.47$  mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> or  $0.00864 \pm 0.0069$  MgC ha<sup>-1</sup> year<sup>-1</sup>. This increment represents a 5.76% increase in water-air interface carbon emissions.

# CH<sub>4</sub> Emission Comparison with other Mangrove Areas

Methane emission in the study area was in the range of worldwide estuary. Other than freshwater sites, methane emission (0.02-0.5 mmol  $m^{-2} day^{-1}$ ) as mentioned by Abril and Borges [20] 0.02-0.5 mmol m<sup>-2</sup> day<sup>-1</sup> and was comparable to the value reported from the Avicennia mangrove site, Can Gio Mangrove Forest, Hochiminh City, Vietnam [3]. The Xuan Thuy methane emission rate in this study was higher than the values reported from Ranong Biosphere Reserve, Thailand [21], Red Sea, Saudi Arabia [22], Rhizophora mangrove site at Can Gio Mangrove Forest, Hochiminh City, Vietnam [23], but lower than those reported values from the Fitzroy River, Johnstone River, and Burdekin River mangrove creeks, Australia [24]; mangrove forest in Ouemo, New Caledonia [25]; Sundarban mangrove ecosystem, state of West Bengal, India [26], and Dongzhaigang National Nature Reserve, China [27] about 2, 6, 9-20, 12 and 27 fold, respectively (Table 4).

# Relations Between CH<sub>4</sub> Fluxes and Environmental Factors

Several environmental factors influence methane  $(CH_4)$  flux rates in mangrove areas. Past research indicates that  $CH_4$  flux rates in these regions vary based on soil temperature, salinity, pH, substrate availability, and the anaerobic environment necessary for methanogenesis due to tidal inundation and agricultural

chemical input [30]. For instance, studies by Hu et al. [31] found a significant positive correlation between water temperature and CH<sub>4</sub> fluxes, while atmospheric pressure displayed the opposite correlation. The study of Poffenbarger et al. [32] on methane emissions in 31 tidal marshes observed a significant log-linear relationship with salinity across different water sources. Other studies [30, 33] demonstrated that higher salinity restricts  $CH_4$ emission due to its inhibitory effect on methanogen activities. Additionally, since CH<sub>4</sub> generation occurs in anaerobic environments, lower Oxidation-Reduction Potential (ORP) inversely affects CH<sub>4</sub> emissions [34]. A study in the mangroves of southeastern China [35] found no significant effect of factors like plant species, tidal position, or soil characteristics on CH<sub>4</sub> efflux, attributing CH<sub>4</sub> emissions to nutrient inputs from anthropogenic activities like aquaculture. On the other hand, methane emissions control factors in mangroves in southeast Mexico were varied by study sites, which were carbon sequestration and soil pH. They both had an inverse relationship with methane emissions [36]. Land use/ land cover changes are also the driving force of CH<sub>4</sub> generation. The research of Das et al. [26] revealed that the highest CH<sub>4</sub> generation area was the mangrovedeforested agricultural lands, while the lowest produced region was the coastal mangrove forested region. This agrees with Zheng et al. [35], who reported that, on average, undisturbed mangrove sites have very low CH4 efflux rates.

The Spearman's rho correlation test revealed a notably positive correlation between  $CH_4$  fluxes and water pH (R = 0.63, p < 0.05), as well as turbidity (R = 0.78, p < 0.01) and a negative correlation with water temperature (R = -0.73, p < 0.05) and TN concentration (R = -0.69, p < 0.05). Our analysis supports the findings of Hernández and Junca-Gómez [39] regarding the correlation between water pH and  $CH_4$  emission, although it contradicts Hu et al.'s [31] correlation between water temperature and  $CH_4$  emission. As per the Smith and Conen [13] equation, which shows an inverse relationship between ambient

Location	Sampling time	$CH_4$ emission (mmol m <sup>-2</sup> day <sup>-1</sup> )	Reference
Dongzhaigang National Nature Reserve, China	2012-2013	0.90±0.34-12.44±5.88 (5.20±1.66)	[27]
Ouemo, New Caledonia	2016-2017	0.004 - 4.13	[28]
Fitzroy River, Johnstone River and Burdekin River mangrove creeks, Australia	2014	0.10 -1.05	[29]
Red Sea, Saudi	2017	$(0.9 - 13.3) \ge 10^3$	[22]
Sundarban mangrove ecosystem, state of West Bengal, India	2020	Pre-monsoonal, 5/2020: 3.84±0.033 Post-monsoonal, 1/2020: 1.86±0.004	[26]
Ranong Biosphere Reserve, Andaman Sea coast of Southern Thailand	2019, 2020	0.059±0.035	[21]
Can Gio Mangrove forest, Hochiminh city, Vietnam	2017	Avicennia mangrove site: 0.01-0.60 Rhizophora mangrove site: 0.02-0.07	[23]
Xuan Thuy, Nam Dinh, Vietnam	2019	0.001-0.649, (0.193±0.154)	Present study

Table 4. Methane emission from different mangrove forests.

Area	Layer (cm)	pН	Salinity	Eh	$\mathrm{NH_4^+}$	NO <sub>3</sub> -	TN	PO4 <sup>3-</sup>	ТР	DOC	TOC
All the sites	Mix	406	.399	133	.490	.161	077	042	218	453	441
	0-5	252	.385	697	.566	.070	056	501	483	197	105
	15-20	469	.424	.329	.510	032	.126	.234	.067	469	399
	35-40	361	203	622	.343	.343	077	.158	039	784*	729*
RG	Mix	829*	086	.257	.371	657	.429	.257	.143	783	943*
	0-5	667	086	729	.600	600	.371	464	086	600	943*
	15-20	886*	086	.200	.314	743	.371	.257	.543	522	771*
	35-40	657*	.371	.771	.086	638	.314	.319	.000	754	841*
RTS	Mix	.429	.714	771	.600	.657	200	.029	522	667	771
	0-5	.486	.786	714	.657	.371	.029	429	486	580	486
	15-20	.319	.406	.257	.714	.486	.086	.493	377	812*	714*
	35-40	.319	371	086	.086	.714	371	.319	143	928*	829*

Table 5. Spearman's rho correlation between  $CH_4$  fluxes and soil quality variables in the study area.

temperature and  $CH_4$  flux, our results appear reasonable. However, we did not find any statistically significant correlation between  $CH_4$  flux and parameters such as DO, salinity, and nutrients ( $NH_4^+$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , and TP) in water samples.

Regarding soil environmental factors influencing CH<sub>4</sub> emission, Spearman's rho test was also applied to each soil layer (0-5 cm, 15-20 cm, 35-40 cm) and a composite sample. The analysis showed a significant negative correlation between CH4 emission and sediment properties like pH, Dissolved Organic Carbon (DOC), and Total Organic Carbon (TOC), as presented in Table 5. Specifically, in the mangrove area, DOC (R = -0.78; p < 0.05) and TOC (R = -0.73; p < 0.05) were significantly inversely correlated with CH<sub>4</sub> emission in the deeper soil layers. A similar negative correlation between DOC, TOC, and CH<sub>4</sub> emission was observed in both the old-stand and young-stand forests, primarily in the middle and deeper layers (-0.94 < R < -0.71; p < 0.05). This indicates that more favorable anaerobic conditions in these layers stimulate methanogens activities, resulting in increased consumption of carbon substrates and the subsequent negative correlation observed between CH4 emission and TOC and DOC in these layers. Additionally, a significant negative correlation between pH and CH<sub>4</sub> emission was found in the old-stand forest, consistent with a previous study [36] reporting a negative relationship between CH<sub>4</sub> emission and soil pH. However, we did not identify statistically significant correlations between other variables like soil salinity, redox potential, nutrients (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3-</sup>, TN and TP), and  $CH_4$  emission.

## Conclusions

The study results offer compelling evidence highlighting the discrepancy between actual methane emissions observed in the Xuan Thuy mangrove area and the default estimations proposed by the IPCC. The observed methane flux rates, notably lower than the default values, cast doubt on the reliability of generic estimations suggested by international guidelines. These findings strongly advocate for precise, sitespecific monitoring methods to ensure accurate assessments of greenhouse gas emissions, particularly within mangrove ecosystems. Additionally, the study emphasizes the intricate relationship between methane emissions and various environmental factors. Factors such as temperature, pH, turbidity, and nitrogen content in water, as well as pH, DOC, and TOC in soil, play significant roles in influencing methane emissions. Understanding these controlling factors is crucial for both understanding and managing greenhouse gas emissions within mangrove ecosystems. Furthermore, this study highlights the potential implications for greenhouse gas inventory and policy development. Relying solely on default values for emissions could lead to substantial overestimations, stressing the need for meticulous and site-specific monitoring practices. The importance of sitespecific data over generic estimations becomes evident in environmental management and policy development, ensuring informed decision-making and accurate assessments. Considering the geographical distribution of Vietnam's mangrove forests across four zones and twelve subzones (North-east coast: three subzones, Northern delta: two subzones, Central coast: three subzones, and Southern delta: four subzones), it becomes imperative to conduct future investigations to provide more precise evaluations of methane gas emissions. Using Tier 2 emission factors, rather than the default Tier 1 emission factors set by the IPCC, for each subzone's mangrove forest can contribute significantly to more accurate estimations of methane emissions.

## Acknowledgments

This research was supported by the Project "*Role of* mud microbial community in the methane emission from mangrove forest of Xuan Thuy National Park" (Project code VAST07.04/19-20).

## **Conflict of Interest**

The authors declare no conflict of interest.

### References

- NGUYEN H.T., NGUYEN S.V., DAU V.H., LE A.T.H., NGUYEN K.V., NGUYEN D.P., BUI X.T., BUI H.M. The nexus between greenhouse gases, economic growth, energy and trade openness in Vietnam. Environmental Technology & Innovation, 28, 102912, 2022.
- 2. VUONG T.K., BUI H.M. The role of corporate social responsibility activities in employees' perception of brand reputation and brand equity. Case Studies in Chemical and Environmental Engineering, **7**, 100313, **2023**.
- DUONG N.T.T., TRUONG T.T.C., BUI H.M. Estimation of Forest Biomass and Absorbed CO<sub>2</sub> by Remote Sensing in Can Gio, Vietnam. Polish Journal of Environmental Studies, 33 (2), 1, 2023.
- HA MANH B., VAN NGUYEN S., HUYNH A.T., HIEP NGHIA B., NGUYEN H.T.T., PERNG Y.S., BUI X.T., NGUYEN H.T. Correlation between nitrous oxide emissions and economic growth in Vietnam: An autoregressive distributed lag analysis. Environmental Technology & Innovation, 29, 102989, 2023.
- 5. PHAM T.D., YOSHINO K. Impacts of mangrove management systems on mangrove changes in the Northern Coast of Vietnam. Tropics, **24** (4), 141, **2016**.
- MURDIYARSO D., KRISNAWATI H., ADINUGROHO W.C., SASMITO S.D. Deriving emission factors for mangrove blue carbon ecosystem in Indonesia. Carbon Balance and Management, 18 (1), 12, 2023.
- WARNER R., KAIDONIS M., DUN O., ROGERS K., SHI Y., NGUYEN T.T.X., WOODROFFE C.D. Opportunities and challenges for mangrove carbon sequestration in the Mekong River Delta in Vietnam. Sustainability Science, 11, 661, 2016.
- HONG HANH N.T., KHANH LINH L., HONG TINH P., DAC TRUONG L., THI THU B., MINH TAM T. Study on Quantification of Carbon Stock in Mangrove Forest along the Coast of Hai Lang Commune, Tien Yen District, Quang Ninh Province. VNU Journal of Science: Earth and Environmental Sciences, 34 (3), 1, 2018.
- PHAM H.T., MAI S.T. Vulnerability to climate change of mangroves in Xuan Thuy National Park, Vietnam. Journal of Agricultural and Biological Science, 10 (2), 55, 2015.
- LIPPS W.C., BRAUN-HOWLAND E.B., BAXTER T.E. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, pp. 2023.
- 11. REARDON J., FOREMAN J.A., SEARCY R.L. New reactants for the colorimetric determination of ammonia. Clinica chimica acta, **14**, 403, **1966**.
- YU H., ORGAN H., XU D., COFFIN R. Tidal control and mangrove dieback impact on methane emissions from a subtropical mangrove estuary. Limnology and Oceanography, 68 (4), 753, 2023.
- SMITH K.A., CRESSER M.S. Measurement of trace gases, I: gas analysis, chamber methods, and related procedures. Soil and Environmental Analysis: CRC Press; pp 394, 2003.
- 14. ARTZ R., SAUNDERS M., YELURIPATI J., POTTS J., ELSTON D., CHAPMAN S. An assessment of the proposed IPCC "2013 Supplement to the 2006 guidelines: Wetlands" for use in GHG accounting of Scottish peatland restoration. CXC briefing, Scottish Government. Revised Version February, 2014.

- 15. LE N.D., NGUYEN T.H., DUONG T.T., ROCHELLE-NEWALL E., HOANG T.T.H., VU T.H., PHAM T.M.H., NGUYEN T.A.H., DINH L.M., PHUNG T.X.B., NGUYEN T.D., PHAM T.M.H., DAO V.H., LE T.P.Q. Risk of eutrophication in the seawater of the coastal Red River aquaculture zone (Thai Binh province, Vietnam). Regional Studies in Marine Science, 55, 102587, 2022.
- LIU J., MYAT T. Contaminants and heavy metals along the mangrove area of Dongzhai Harbor, China: distribution and assessment. SN Applied Sciences, 3 (10), 823, 2021.
- 17. WANG F., CHEN N., YAN J., LIN J., GUO W., CHENG P., LIU Q., HUANG B., TIAN Y. Major Processes Shaping Mangroves as Inorganic Nitrogen Sources or Sinks: Insights From a Multidisciplinary Study. Journal of Geophysical Research: Biogeosciences, **124** (5), 1194, **2019**.
- WIGAND C., OCZKOWSKI A.J., BRANOFF B.L., EAGLE M., HANSON A., MARTIN R.M., BALOGH S., MILLER K.M., HUERTAS E., LOFFREDO J., WATSON E.B. Recent Nitrogen Storage and Accumulation Rates in Mangrove Soils Exceed Historic Rates in the Urbanized San Juan Bay Estuary (Puerto Rico, United States). Frontiers in Forests and Global Change, 4, 2021.
- HIEN T.H. Quantitative study on carbon stock and flux in planted mangroves at Xuan Thuy National Park. Ha Noi, Vietnam: Thuyloi University; 2018.
- TREMBLAY A. Greenhouse gas emissions-fluxes and processes: hydroelectric reservoirs and natural environments, Springer Science & Business Media, pp. 2005.
- KITPAKORNSANTI K., PENGTHAMKEERATI P., WORACHANANANT P., LIMSAKUL A. Soil Nitrogen Stock of Primary and Restored Mangrove Forests in Ranong Biosphere Reserve, Thailand. Journal of Fisheries and Environment, 46 (3), 108, 2022.
- 22. SEA M.A., GARCIAS-BONET N., SADERNE V., DUARTE C.M. Carbon dioxide and methane fluxes at the air-sea interface of Red Sea mangroves. Biogeosciences, 15 (17), 5365, 2018.
- DUŠEK J., NGUYEN V.X., LE T.X., PAVELKA M. Methane and carbon dioxide emissions from different ecosystems at the end of dry period in South Vietnam. Tropical Ecology, 62 (1), 1, 2021.
- ROSENTRETER J.A., MAHER D.T., ERLER D.V., MURRAY R.H., EYRE B.D. Methane emissions partially offset "blue carbon" burial in mangroves. Science Advances, 4 (6), eaao4985 2018,
- 25. JACOTOT A., MARCHAND C., ALLENBACH M. Tidal variability of CO2 and CH4 emissions from the water column within a Rhizophora mangrove forest (New Caledonia). Science of The Total Environment, 631-632, 334, 2018.
- 26. DAS N., CHAKRABORTTY R., PAL S.C., MONDAL A., MANDAL S. A novel coupled framework for detecting hotspots of methane emission from the vulnerable Indian Sundarban mangrove ecosystem using data-driven models. Science of The Total Environment, 866, 161319, 2023.
- 27. HE Y., GUAN W., XUE D., LIU L., PENG C., LIAO B., HU J., ZHU Q.A., YANG Y., WANG X., ZHOU G., WU Z., CHEN H. Comparison of methane emissions among invasive and native mangrove species in Dongzhaigang, Hainan Island. Science of The Total Environment, 697, 133945, 2019.
- JACOTOT A., MARCHAND C., ALLENBACH M. Biofilm and temperature controls on greenhouse gas (CO2 and CH4) emissions from a Rhizophora mangrove soil (New Caledonia). Science of The Total Environment, 650, 1019, 2019.
- 29. ROSENTRETER J.A., MAHER D.T., ERLER D.V., MURRAY R., EYRE B.D. Seasonal and temporal CO2 dynamics in three tropical mangrove creeks – A revision

of global mangrove CO2 emissions. Geochimica et Cosmochimica Acta, **222**, 729, **2018**.

- CHAUHAN R., DATTA A., RAMANATHAN A.L., ADHYA T.K. Factors influencing spatio-temporal variation of methane and nitrous oxide emission from a tropical mangrove of eastern coast of India. Atmospheric Environment, **107**, 95, **2015**.
- HU J., GUAN W., CHEN H. Methane Emissions from Surface of Mangrove River on Hainan Island, China. Atmosphere, 12 (9), 2021.
- 32. POFFENBARGER H.J., NEEDELMAN B.A., MEGONIGAL J.P. Salinity Influence on Methane Emissions from Tidal Marshes. Wetlands, 31 (5), 831, 2011.
- 33. ROSENTRETER J.A., MAHER D.T., ERLER D.V., MURRAY R., EYRE B.D. Factors controlling seasonal CO2 and CH4 emissions in three tropical mangrove-dominated estuaries in Australia. Estuarine, Coastal and Shelf Science, 215, 69, 2018.

- LIN C.-W., KAO Y.-C., CHOU M.-C., WU H.-H., HO C.-W., LIN H.-J. Methane Emissions from Subtropical and Tropical Mangrove Ecosystems in Taiwan. Forests, 11 (4), 00470, 2020.
- 35. ZHENG X., GUO J., SONG W., FENG J., LIN G. Methane Emission from Mangrove Wetland Soils Is Marginal but Can Be Stimulated Significantly by Anthropogenic Activities. Forests [Internet]. 9 (12), 738 2018.
- 36. AGRAZ-HERNÁNDEZ C.M., CHAN-KEB C.A., MUÑIZ-SALAZAR R., PÉREZ-BALAN R.A., OSTI-SÁENZ J., GUTIÉRREZ-ALCÁNTARA E.J., REYES-CASTELLANO J.E., MAY-COLLI L.O., CONDE-MEDINA K.P., RUIZ-HERNÁNDEZ J. Relationship between blue carbon and methane and the hydrochemistry of mangroves in southeast Mexico. Applied Ecology & Environmental Research, 18 (1), 1091, 2020.