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Assessment of Methane Variability from Natural Wetlands of Uttar Pradesh, India-Implications for Tropical Countries

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ABSTRACT

Tropical wetlands are one of the most dynamic natural sources of atmospheric methane (CH_4) but the CH_4 emission data is still scanty to quantify and elaborate the process of CH_4 emissions from natural freshwater tropical wetlands. In view of this, the present study attempts to estimate the CH_4 emissions from two natural tropical wetlands of Uttar Pradesh, India to further augment the CH_4 emission database for tropical countries for improved understanding of CH_4 cycling in tropical wetlands. This study elucidates the importance of temporal, site specific and zone-wise dependence of CH_4 emission in a wetland. Significantly higher CH_4 flux in the summer season than monsoon and winter season at both the locations ($p<0.05$ for shallow water, deep water and exposed wetland soil zone) clearly define the importance of temperature, water depth, dissolved oxygen, redox potential, biological oxygen demand and plant biomass in regulating the seasonal CH_4 flux. Spatial analysis revealed that higher mean annual CH_4 flux from the Nawabganj lake (153.5±23.2 mg m^{-2} day^{-1}) as compared to the Keetham lake (80.0±11.8 mg m^{-2} day^{-1}), is attributed to enhanced anoxic conditions at Nawabganj lake owing to shallow, static and shrinking water base, high plant mediated CH_4 flux and boosted autochthonous organic matter production by dense aquatic vegetation present in the lake chiefly including *Eleocharis dulcis*, *Nelumbo nucifera*, *Ipomoea aquatica*. Zone-wise, shallow water zone contributes maximum to CH_4 flux than deep water and exposed wetland soil zones at both the sites due to high biological oxygen demand, heavy vegetation infestation and decreased values for water depth, dissolved oxygen and redox potential.

Key words: Methane flux, wetland, soil organic carbon, macrophyte, chamber technique

INTRODUCTION

Global warming and its mitigation have become one of the most important environmental issues with the increasing quantity of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chloro-fluoro carbons (CFCs), water vapour etc., in the atmosphere. Methane (CH_4) is the third most important greenhouse gas after CO_2 and water vapour and its mixing ratio is continuously increasing from 1.76 ppm in 2004 (WCR., 2007) to 1.8 ppm in 2011 (Hartmann *et al*., 2014). This rising trend of CH_4 concentration in the atmosphere is of great concern worldwide as the global warming potential of CH_4 is 28 times higher than CO_2 (Myhre *et al*., 2014). Thus, CH_4 emission estimation is imperative to understand CH_4 emission patterns around the world.

Wetlands, the biggest natural source of CH_4 emission, contribute to about 25% of the global CH_4 budget in the atmosphere (Wuebbles and Hayhoe, 2002), of which 50-60% is contributed by natural tropical wetlands (Cao *et al*., 1996; Bloom *et al*., 2010). Aselmann and Crutzen (1989) have observed that tropical wetlands emit about 42 Tg of CH_4 year^{-1} thus, contributing about 38% of the global wetland CH_4 emissions. However, there is no unanimity among researchers about the quantitative contribution of CH_4 emission from tropical wetlands. Bergamaschi *et al*. (2007) and Mitsch *et al*. (2010) reported that about 76% (138 Tg year^{-1}) of global wetland CH_4 (180 Tg year^{-1}) is imparted by tropical wetlands. As per recent estimates, annual tropical wetland CH_4 emissions have increased by 3.4 Tg year^{-1} between 2003 and 2009 accounting for about 111.1 Tg of CH_4 year^{-1} (Bloom *et al*., 2012). This is primarily due to the fact that CH_4 emission rates from natural tropical/subtropical wetlands vary considerably leading to large uncertainties in the atmospheric CH_4 budget due to temporal, spatial and geographical differences.

The problem is further compounded by the lack of extensive CH_4 emission studies in the high density wetland areas such as Indo-Gangetic plains in India. India exhibits a great physiographical diversity and accordingly wetlands exist in all geographical zones (Garg, 2015). Thus, being a tropical/sub-tropical country, Indian studies can be of pivotal importance in assessing the CH_4 emissions from natural tropical/subtropical wetlands. In the Indian subcontinent, most of the work has been reported from saline wetlands, including mangroves (Purvaja *et al*., 2004; Krithika *et al*., 2008), lagoons (Verma *et al*., 2002) and coastal estuaries (Shalini *et al*., 2006; Rajkumar *et al*., 2008). However, very few CH_4 emission studies have been reported from natural tropical/ subtropical freshwater wetlands (Dutta and Mallick, 2009; Khoiyangbam *et al*., 2007; Singh *et al*., 2000). Thus, considering the lack of substantial CH_4 flux data from Indian tropical/subtropical freshwater wetlands, present study estimates spatial (site specific and zone-wise) and temporal CH_4 emissions from two different types of natural freshwater wetlands viz., Keetham lake, Agra and Nawabganj lake, Unnao located in the tropical zone of India. This will be immensely helpful in preparation of regional and global greenhouse gas emission budgets.

MATERIALS AND METHODS

Experimental sites: The experimental sites selected to carry out the present research work comprises of two natural wetlands located in the state of Uttar Pradesh, India: Keetham lake, a freshwater pentagonal oxbow lake located inside Soor Sarovar Bird Sanctuary, Agra and Nawabganj lake, a marshy/swampy freshwater lake which lies in Nawabganj Bird Sanctuary, Unnao. Important features related to study sites are mentioned in Table 1 and the location of study sites is shown in Fig. 1.

Keetham lake is a deep flowing water system consisting of both shallow and stratified deep areas. The input water in Keetham lake is obtained from Agra canal originating from the Okhla

Table 1: Important feature of study sites

	Sites	
Features	Keetham lake	Nawabganj lake
Coordinates	27°15.287'N, 77°50.386'E	26°37.094'N, 80°39.259'E
Type	Natural	Natural
Total area (ha)	300	225
Flowing/stagnant	Flowing	Stagnant
Annual water depth (m)	0.15-8	0.15-1.9
Vegetation density/soil	Sparse/moist with high sand content	Dense/dry with high clay content

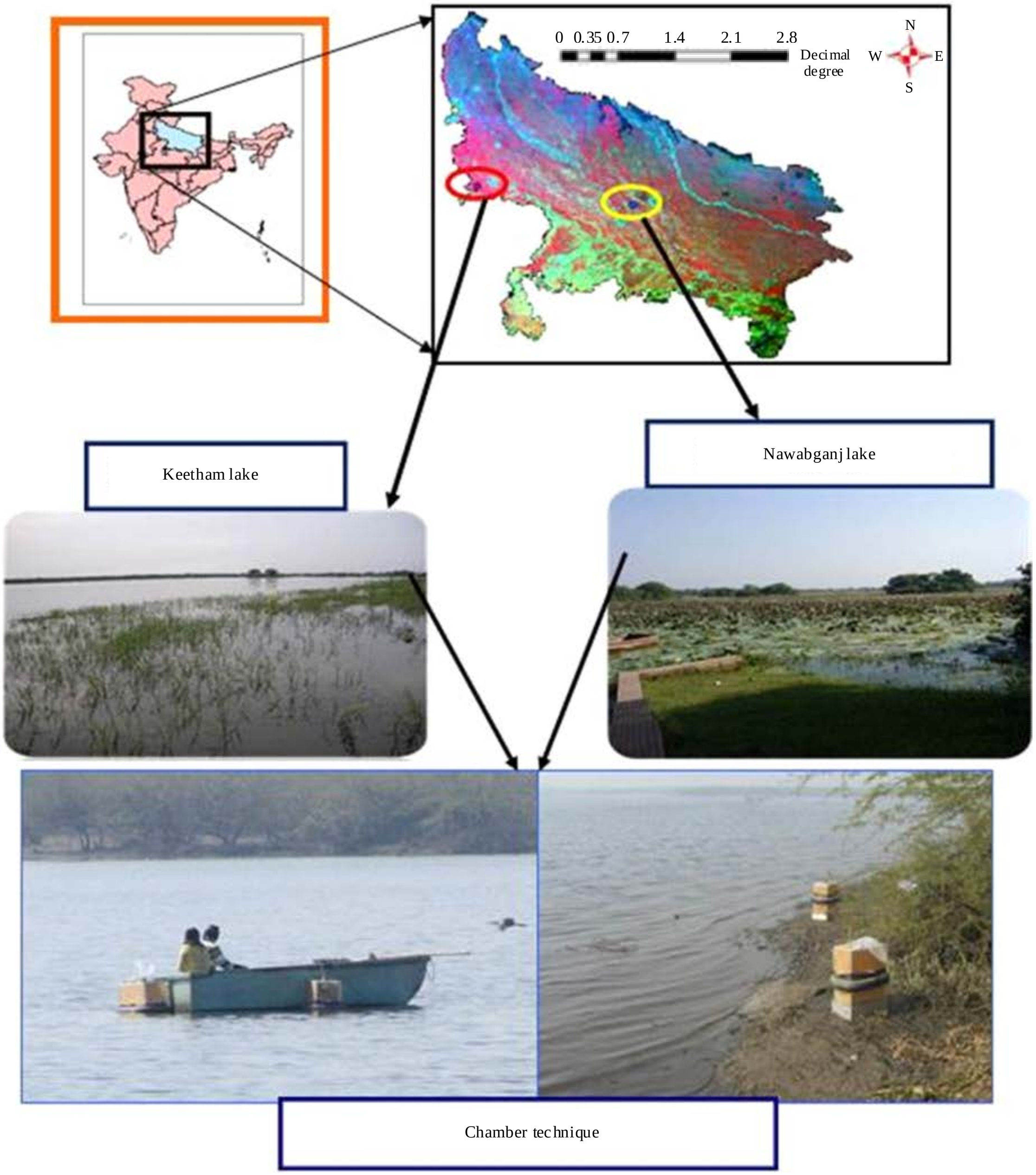


Fig. 1: Study area showing experimental sites and chamber technique used for CH_4 gas sampling

barrage on river Yamuna near Delhi along with rainfall and surface runoff from the nearby areas. Extra water from the Keetham lake is diverted for Mathura refinery for treatment processes and the rest of the water gets released into the river Yamuna heading towards the Agra city. On the other hand, Nawabganj lake is shallow and static water system which has been fed by a tube well/ irrigation canal along with rain water to maintain the oxic conditions within the lake. But due to increased irrigational needs and construction of infrastructure in the nearby areas, canal water supply has reduced. As a result of this, water base of the lake is shrinking and getting more anoxic in the absence of supply of fresh oxic water.

Sample collection and analysis: To find out spatial variability within the lake and to facilitate systematic sample collection and better data interpretation, each lake was divided into two zones, namely, the Exposed Wetland Soil Zone (EWSZ) and the Water Zone (WZ). The EWSZ incorporates water saturated soils located just adjacent to the lake edges, comparatively dry soils located few meters away from the lake periphery and the soil present in the lake which gets exposed during summers due to drying of the lake. The WZ was further divided into two zones: Shallow water zone (SWZ: Depth up to 150 cm for both the sites) and deep water zone (DWZ: Depth up to 800 cm in Keetham lake and 190 cm for Nawabganj lake) for collection and analysis of CH_4, water, soil and vegetation samples. It may be mentioned that in the Nawabganj lake, water depth decreased noticeably during summers (range: 15.01-45.23 cm) and therefore, samples were collected for two water levels up to 15 and 45 cm. CH_4 emission measurements were carried out for three distinct seasons for both the wetlands, i.e., monsoon (July to October, 2010), winter (November to February, 2010-2011) and summer (March to June, 2011). Gas samples were collected in 3-4 replicates twice a day and once in a season for each zone.

CH_4 gas sampling and analysis: CH_4 gas samples were collected using the Chamber Technique. Two different types of chambers were deployed for gas sample collection, namely, (a) Floating chambers for water surface and (b) Static chambers for soil surface (Fig. 1). Pre-evacuated 50 mL air tight plastic syringes provided with three-way stopcocks were deployed to collect gas samples at the intervals of 0, 15, 30, 45 and 60 min.

Gas samples were analyzed in the laboratory within a week of gas sampling using a Gas Chromatograph (model No. 6890, Agilent Technologies, USA) provided by a Flame Ionization Detector (FID) and wide bore HP-PLOT Q capillary column. Methane (CH_4) gas concentration in sample was calculated by comparing it with standard CH_4 in nitrogen (1.8±0.2 ppmv CH_4 in nitrogen procured from MAINZ, Germany and 10.1±0.1 ppmv CH_4 in nitrogen obtained Spectra Gas, USA) deploying the equation used by Singh *et al.* (1998) and Chakraborty *et al.* (2011):

$$CH_4\ (\text{mg m}^{-2}\ \text{day}^{-1}) = \frac{BV_{STP} \times C_{CH_4} \times M \times 1000 \times 60}{10^6 \times 22400 \times A \times t} \times 24$$

Where:

$$BV_{STP} \text{ is box air volume in cm}^3 \text{ at standard temperature and pressure} = \frac{BV \times BP \times 273}{(273+T) \times 760}$$

$$\text{BV (Box volume) for water surface} = (H-h) \times L \times W\text{-Volume of biomass inside the chamber}$$

where, H is chamber height in cm, h is water level above the channel, L is chamber length in cm, W is chamber width in cm.

$$\text{BV (Box volume) for soil surface} = (H+h) \times L \times W\text{-Volume of biomass inside the chamber}$$

where, H is chamber height in cm, h is channel height above soil surface in cm, L is chamber length in cm, W is chamber width in cm, M is molecular weight of CH_4, BP is barometric pressure (mm Hg) at the time of sampling, T is chamber air temperature at the time of sampling in Kelvin (K; 273+temp in °C), t is sampling time intervals of 0, 15, 30, 45 and 60 min, C_{CH_4} is Change in CH_4 concentration in (ppm) from 0 to t min sampling and A is wetland area covered by the chamber in m^2

Methods for collection and analysis of water, soil and vegetation composition: Water samples were collected in 2 L plastic bottles and soil samples were collected in air tight plastic vials using soil tube auger (Singh *et al*., 1999) at the depth varying from 18-19 cm in triplicates to analyze various water and soil quality parameters. Water Depth (WD), Water Temperature (WT), Soil Temperature (ST), pH and Eh (redox potential) for water and soil samples were also recorded at the time of CH_4 flux withdrawal. All the water samples were preserved at 4°C in an ice box/refrigerator for analysis. Biological Oxygen Demand (BOD) for water samples was estimated within 6-8 h of storage, whereas, nitrate (NO_3^-), sulfate (SO_4^{2-}) and Total Organic Carbon (TOC) contents of water were measured within a week of water sampling. On the other hand, Soil Organic Carbon (SOC) and soil texture were measured within 15 days of soil sampling as the soil exhibits relatively stable physico-chemical properties as compared to water.

Sampling point locations were collected using a GARMIN etrex-12 channel global positioning system. In order to determine the vegetation characteristics, samples were collected from 1×1 m^2 plots using quadrat method (APHA., 1995) in self sealing plastic bags. Plant biomass was estimated within 4-5 days of sampling. Fresh weight of plant samples was recorded in the field using battery operated digital weighing balance, whereas, the dried weight of each plant species was measured by oven drying the samples at 70°C till constant weight. Methods used for analyzing various water, soil and vegetation characteristics are summarized in the Table 2.

Statistical analysis: Pearson correlation was used as a measure to understand the dependence of CH_4 emissions on water, soil and vegetation parameters. Spatial and temporal variability in CH_4 emissions at both the study sites was evaluated by non-parametric statistics depending upon the CH_4 data distributions using SPSS-12.0 statistical software for Windows.

In case of EWSZ, though the spatial CH_4 values achieved homogeneity of variances (Levene's Test for Equality of Variances; $p>0.05$) but did not exhibit the normal distribution (Kolmogorov-Smirnov Test; $p<0.05$). On the contrary, temporal CH_4 values neither exhibited normal distribution (Kolmogorov-Smirnov Test; $p<0.05$) nor achieved homogeneity of variances (Levene's Test for Equality of Variances; $p<0.05$).

Table 2: Techniques used for analyzing different water, soil and vegetation parameters

Parameters	Analytical technique used
Water DO, Eh and pH of soil and water	Portable DO, Eh and pH meter (HACH-HQ30D)
Water and soil temperature	Portable infra red thermometer (OAKTON: Infra Pro 5)
Water phosphate	Stannous chloride method (APHA., 1995)
Water and soil nitrate	Phenol di-sulphonic acid (APHA., 1995)
Water and soil sulfate	Turbidimetric method (APHA., 1995)
Water depth	Well marked wooden-pole
Water BOD	Modified winkler method (APHA., 1995)
Total organic carbon	HACH total organic carbon analyzer
Soil organic carbon	Walkley and black method (Walkley and Black, 1934)
Plant biomass	Harvest method (APHA., 1995)
Soil texture	Bouyoucos hydrometer method (Singh *et al*., 1999)

HACH total organic carbon analyzer consisted of two units including (a) Digester (model: HACH-DRB 200) to digest the samples and (b) Calorimeter (model: HACH-DR 900) to read the samples

For WZ, both the spatial and temporal CH_4 values did not satisfy the conditions of normal distribution (Kolmogorov-Smirnov Test; $p<0.05$ for both spatial and temporal CH_4 values) and homogeneity of variances (Levene's Test for Equality of Variances; $p<0.05$ for both spatial and temporal CH_4 values). Consequently, non-parametric statistics including Mann-Whitney U-test has been applied to assess the spatial variability, whereas Kruskal-Wallis H-test has been deployed to evaluate the temporal variability in CH_4 emissions in both the zones i.e., WZ and EWSZ.

RESULTS AND DISCUSSION

Methane (CH_4) flux estimation: The present study represents the first ever CH_4 emission data for Keetham lake and updated CH_4 emission data for Nawabganj lake for improved understanding of CH_4 emissions from natural tropical/subtropical wetlands. From Keetham lake, the mean annual CH_4 flux was about 122.3±20.0 mg m^{-2} day^{-1} for SWZ, 17.3±3.1 mg m^{-2} day^{-1} for DWZ and 75.7±18.7 mg m^{-2} day^{-1} for EWSZ. Likewise, in case of Nawabganj lake, the mean annual CH_4 flux values were observed as 300.1±62.9, 146.6±18.9 and 56.7±11.7 mg m^{-2} day^{-1} for SWZ, DWZ and EWSZ, respectively. The estimated seasonal CH_4 flux values for both the sites are represented in Fig. 2. CH_4 flux at both the locations was highest during summer season as compared to monsoon and winter season. Seasonal CH_4 emission variations were mainly controlled by parameters such as temperature, Eh, WD, DO, BOD and plant biomass.

Results have also brought out that the Nawabganj lake was found to emit higher mean annual CH_4 flux as compared to Keetham lake (Table 3) owing to (1) Shrinking water base at Nawabganj lake with decreased WD, low DO and Eh values leading to enhanced anoxic conditions,

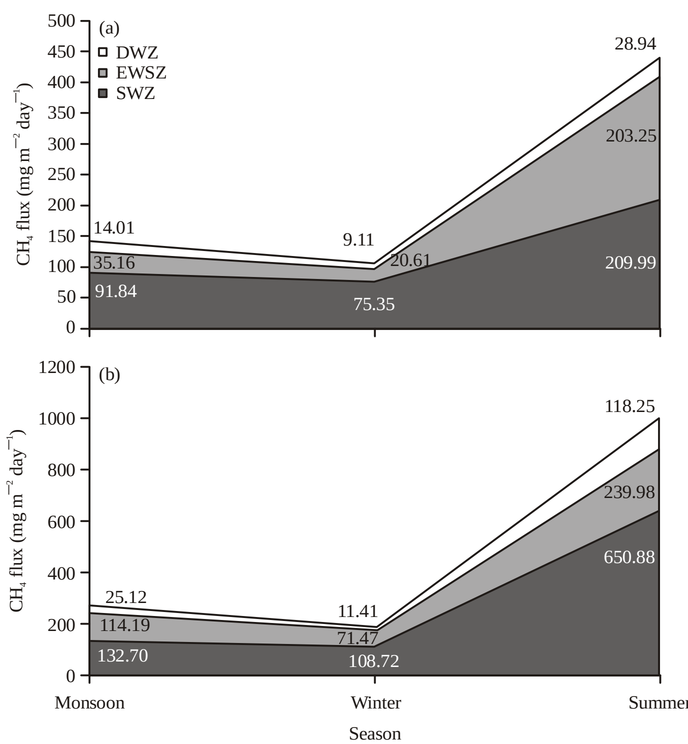


Fig. 2(a-b): Temporal variations in CH_4 emissions at (a) Keetham lake, Agra and (b) Nawabganj lake, Unnao

Table 3: Estimation of CH_4 flux at both the study sites

	Annual mean CH_4 flux (mg m^{-2} day^{-1})	
Zones	Keetham lake	Nawabganj lake
Shallow Water Zone (SWZ)[a]	122.3±20.0	300.1±62.9
Deep Water Zone (DWZ)[b]	17.3±3.1	146.6±18.9
Exposed Wetland Soil Zone (EWSZ)[c]	75.7±18.7	56.7±11.7
Net CH_4 flux (mg m^{-2} day^{-1})[d]	80.0±11.8	153.5±23.2

[a]Sample size (n) for SWZ: n = 20 for Keetham lake and n = 18 for Nawabganj lake, [b]Sample size (n) for DWZ: n = 12 for Keetham lake and n = 18 for Nawabganj lake, [c]Sample size (n) for EWSZ: n = 22 for Keetham lake and n = 26 for Nawabganj lake, [d]Complete sample size (n) for Keetham lake n = 54 and for Nawabganj lake n = 62

(2) High BOD values supporting increased biological activities for CH_4 generation and (3) High plant mediated CH_4 vascular transport and high availability of labile plant substrates contributed by accelerated autochthonous organic matter production by intense aquatic vegetation present throughout the lake. In contrast, though the Keetham lake receives high allochthonous organic loadings (indicated by high TOC values) from Yamuna and Hindon river via Agra canal, it exhibited low CH_4 emission potential. This observation was presumably due to the fact that the Keetham lake is a flowing and deep freshwater lake characterized by low autochthonous organic matter production, low BOD and high DO values because of well oxygenated conditions at high WD.

CH_4 emissions analysis among all three zones showed that SWZ was found to emit maximum CH_4 flux at both the sites (Table 3). The plausible explanations for this observation include: (a) High diffusive flux as SWZ is a non-stratified zone where CH_4 directly diffuses out into the atmosphere without getting oxidized in oxic epilimnion, (b) High plant mediated CH_4 flux due to the heavy macrophytic infestations and most of the CH_4 entering the plant roots escape directly from rhizosphere to the atmosphere without any oxidation, (c) Increased annual averaged Aquatic Plant Biomass (APB) in SWZ than in DWZ at both the sites providing the enhanced availability of plant substrates to methanogens to support high CH_4 flux values and (d) More favourable hydrological characteristics including high BOD, low WD and low Eh values for SWZ in comparison to DWZ at both the sites.

Methane (CH_4) flux for DWZ at Keetham lake was less in comparison to SWZ because in stratified deep water without of vegetation cover, surface water is normally oxic and nearly 90% of CH_4 emitted get oxidized before reaching the atmosphere leading to decreased CH_4 flux. Similar findings have also been reported by King (1990) and Laanbroek (2010). On the other hand, EWSZ was found to be the second largest contributor to the averaged CH_4 flux at the Keetham lake indicating that the vegetated soil surfaces emitted more CH_4 than non-plant open DWZ. In contrast, the least contribution by EWSZ to CH_4 flux at Nawabganj lake supports the importance of aquatic vegetation in regulating CH_4 emissions over semi-aquatic/terrestrial vegetation of surrounding soils.

Therefore, CH_4 variability among different zones, varied as SWZ>EWSZ>DWZ at Keetham lake and SWZ>DWZ>EWSZ at Nawabganj lake. Thus, in the present study, the mean annual CH_4 flux values for entire Keetham lake (80.0±11.8 mg m^{-2} day^{-1}) and Nawabganj lake (153.5±23.2 mg m^{-2} day^{-1}) were estimated by averaging the CH_4 flux values obtained from three different zones (SWZ, DWZ and EWSZ). Conversely, Singh *et al.* (2000) reported CH_4 emission from single zone (vegetated water surface) as the averaged CH_4 flux for the entire Nawabganj lake to assess the seasonal dynamics of CH_4 flux without considering zone-wise CH_4 variations. But as each zone has its own contribution to the averaged CH_4 flux emitted from an entire wetland area, considering CH_4 flux for one zone as averaged CH_4 flux for entire lake or wetland is not appropriate. Single zone value not only under/overestimate the results but also cannot reflect contribution of different zones existing within the lake. Therefore, for more accurate and reliable measurements, zone-wise dependence of CH_4 emissions should be taken into consideration in all CH_4 estimation studies from wetlands.

Spatial and temporal variations in CH_4 flux for Exposed Wetland Soil Zone (EWSZ): Wetland soils present in both the lakes were alkaline and organic in nature. Keetham lake exhibited moist sandy soil with low Soil Temperature (ST) whereas, soil at Nawabganj lake was comparatively dry with high ST and clay content. Analysis of CH_4 variability in EWSZ showed that the temporal CH_4 concentration variability in EWSZ (Fig. 2) was observed to be significant ($p<0.05$) with maximum CH_4 flux during summer season as compared to monsoon and winter season. On the other hand, no significant spatial pattern was observed for EWSZ ($p>0.05$) as the CH_4 flux obtained from EWSZ in Keetham lake i.e., 75.7±18.7 mg m^{-2} day^{-1} (n = 22) was nearly close to that of EWSZ in Nawabganj lake i.e., 56.7±11.7 mg m^{-2} day^{-1} (n=26). Results opined that the redox potential (Eh) and Soil Temperature (ST) were found to be dominant factors in controlling CH_4 emissions in EWSZ as these parameters showed significant correlations with CH_4 emissions.

It was observed that Eh showed strong negative correlation with CH_4 flux (r = -0.82; $p<0.01$). Thus, EWSZ at Keetham lake released high CH_4 flux as the soil zone at Keetham lake exhibited more reduced conditions with low Eh values (ranging from -126.6 to -50.4 mV with an annual mean value of -83.4±6.6 MV; n = 22) in comparison to Nawabganj lake (ranging from -102.3 to -37.7 mV with annual mean value of -71.7±5.4 mV; n = 26). It was consistent with the fact that soils with lower Eh values are prone to anaerobiosis and enhanced CH_4 generation. In contrast, soil at Nawabganj lake was more oxidized with high Eh values supporting less CH_4 flux. In addition to this, clay content in soil of Nawabganj lake was higher (Fig. 3) than Keetham lake which may favour the trapping of CH_4 bubbles in the soil and decreases CH_4 emissions (Sass *et al*., 1992). Analogous results were also obtained by Sass and Fisher Jr. (1994) as they reported the negative correlation between clay content and CH_4 emissions. Further, low Eh values in summer season clearly justified the negative correlation of Eh with CH_4 flux seasonally and support high CH_4 flux observed for summer season.

The annual averaged ST values were also found within the congenial range of about 25-35°C for methanogenesis in both the wetlands (Fig. 4-5) and exhibited a positive correlation (r = 0.55; $p<0.01$) with CH_4 emissions. The higher CH_4 flux was observed during summer season indicating a major influence of soil temperature in methanogenesis. Increased temperature during summers supported the increased microbial activity and high decomposition rates in wetland soils leading to enhanced CH_4 production.

Above Ground Plant Biomass (AGPB), soil pH and SOC have shown insignificant correlations (r = -0.13; $p>0.05$ for AGPB; r = -0.24; $p>0.05$ for soil pH; r = 0.09; $p>0.05$ for SOC) with CH_4 flux as their annual averaged values did not varied much spatially (Fig. 4, 5 and Table 4, 5). Temporally, AGPB also did not follow any specific trend with CH_4 flux. At Nawabganj lake, AGPB was found to be highest during summer season supporting high CH_4 flux. In contrast, at Keetham lake, AGPB was higher during monsoon season than summer season as the plant species including *Alternanthera paronychioides*, *Polygonum lanigerum*, *Cyperus pygmaeus* and *Rumex dentatus* got degraded during summer season due to the elevated temperature and water scarcity. Almost constant pH and SOC values throughout the year amply indicate that the soil pH and SOC are stable chemical properties that do not fluctuate seasonally.

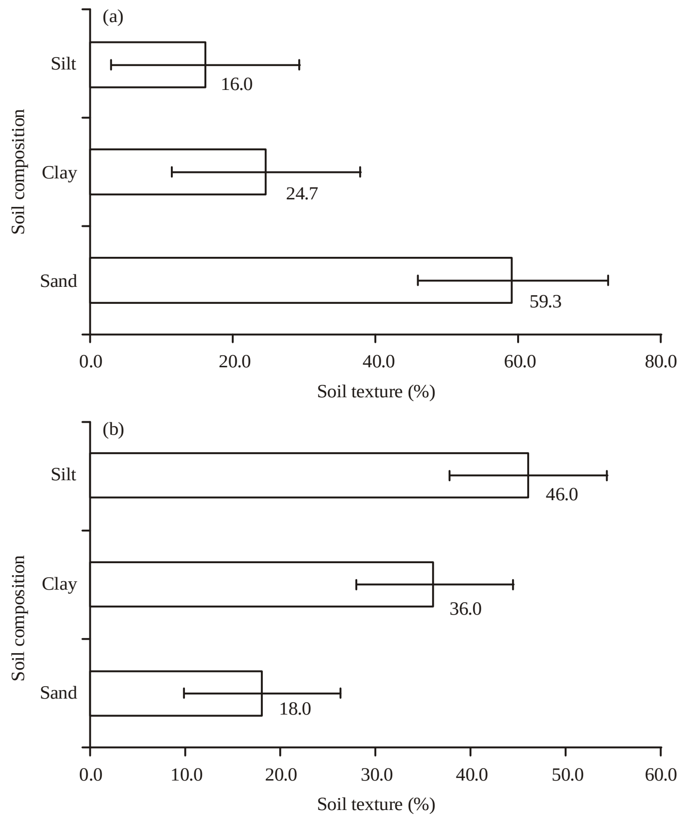


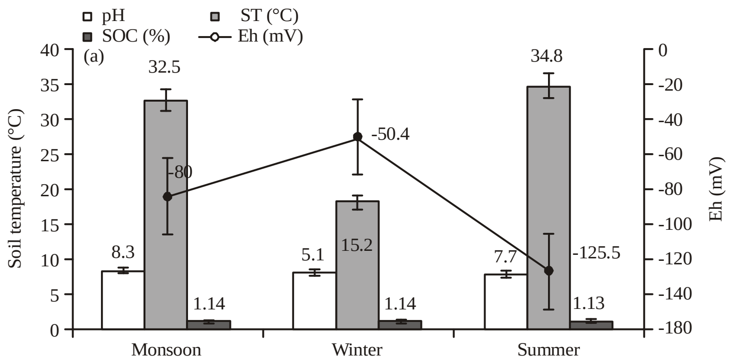
Fig. 3(a-b): Soil composition observed at (a) Keetham lake, Agra and (b) Nawabganj lake, Unnao

Table 4: Floral composition observed at Keetham lake, Agra

	Monsoon		Winter		Summer		
Zones	Floral composition[a,n]	AGPB/APB[b] (g DW m^{-2})[c]	Floral composition[a,n]	AGPB/APB[b] (g DW m^{-2})[c]	Floral composition[a,n]	AGPB/APB[b] (g DW m^{-2})[c]	Annual average[d]
EWSZ	1, 2, 3, 4, 5, 6, 7, 8, 9	26.9	1,7,8,10,11,12,13	18.9	1, 2, 6, 7, 9, 12, 13	23.6	23.1±2.3
SWZ	2, 4, 10, 14	20.3	10,12,15	7.4	9, 10, 12	17.3	15.0±3.9
DWZ	- -	-	-				

[a]Floral composition include: 1: *Prosopis juliflora* (n = 3), 2: *Phyla nodiflora* (n = 4), 3: *Alternanthera paronychioides* (n = 1), 4: *Polygonum lanigerum* (n = 2), 5: *Cyperus pygmaeus* (n = 1), 6: *Paspalum paspalodes* (n = 2), 7: *Cynodon dactylon* (n = 3), 8: *Rumex dentatus* (n = 2), 9: *Alternanthera sessilis* (n = 6), 10: *Paspalum distichum* (n = 5), 11: *Parthenium hysterophorus* (n = 1), 12: *Polygonum glabrum* (n = 5), 13: *Alternanthera philoxeroides* (n = 2), 14: *Echinochloa crusgalli* (n = 1), 15: *Typha elephantina* (n = 1), [b]AGPB/APB: Above ground plant biomass for EWSZ: Exposed wetland soil zone and APB: Aquatic plant biomass for SWZ: Shallow water zone and DWZ: Deep water zone [c]g Dw m^{-2}: Grams of dry weight per meter square, [d]Mean values±standard error, [n] Sample size for each plant species

Spatial and temporal variations in CH_4 emissions for Water Zone (WZ): Spatial and temporal assessment of CH_4 variability for WZ showed that both the locations display significant spatial patterns ($p<0.05$) as Nawabganj lake exhibited higher annual averaged CH_4 flux (223.4±34.9 mg m^{-2} day^{-1}; n = 36) for entire WZ as compared to Keetham lake (83.0±15.4 mg m^{-2} day^{-1}; n = 32). Like EWSZ, temporal CH_4 emission in WZ was also found to be significantly higher for summer season followed by monsoon season and least during winter season ($p<0.05$) at both the sites. The current study demonstrated that in WZ, CH_4 production rate was mainly contingent on WD, DO, BOD, WT, Eh, pH and aquatic plant biomass as these variables were found to be significantly correlated with CH_4 flux. On the other hand, annual mean values for



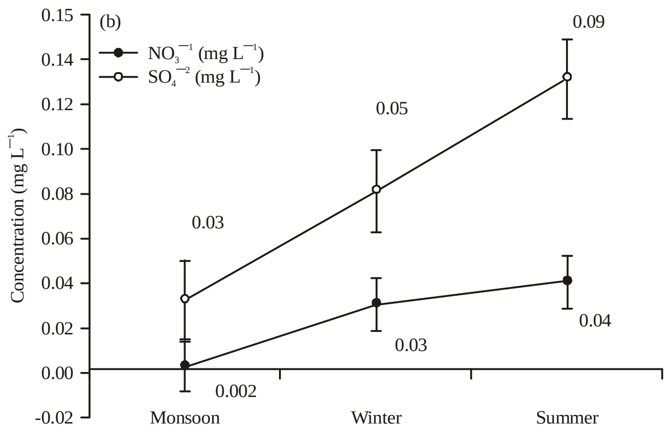


Fig. 4(a-b): Soil characteristics of Keetham lake, Agra (a) Seasonal variability in soil pH, Soil Temperature (ST), Soil Organic Carbon (SOC) and Soil Redox Potential (Eh) to justify the seasonal CH_4 flux variations and (b) shows that the Nitrate (NO_3^-) and sulfate (SO_4^{2-}) contents in all the seasons were well below the moderately inhibitory range of 50 mg L^{-1} for NO_3^- and 500 mg L^{-1} for SO_4^{2-} for methanogenic bacteria

Table 5: Floral composition observed at Nawabganj lake, Unnao

Zones	Monsoon		Winter		Summer		
	Floral composition[a, n]	AGPB/APB[b] (g DW m^{-2})[c]	Floral composition[a, n]	AGPB/APB[b] (g DW m^{-2})[c]	Floral composition[a, n]	AGPB/APB[b] (g DW m^{-2})[c]	Annual average[d]
EWSZ	1, 2, 3, 4, 5, 6, 7	13.2	1, 2, 3, 7, 8, 9, 10, 11	12.2	1, 2, 3, 4, 7, 12, 13, 14, 15, 16, 21, 22	46.8	24.1±11.4
SWZ	14, 15, 16, 17, 18	25.3	14, 16, 18, 19, 22	14.3	14, 15, 16, 18	14.8	18.1±3.6
DWZ	15, 20	11.2	15, 20	7.2	15, 20	12.7	10.4±1.7

[a]Floral composition include: 1: *Parthenium hysterophorus* (n = 3), 2: *Cynodon dactylon* (n = 3), 3: *Cyperus rotundus* (n = 3), 4: *Vernonia cinerea* (n = 2), 5: *Oplismenus burmannii* (n = 1), 6: *Lindernia nummulariifolia* (n = 1), 7: *Ageratum conyzoids* (n = 3), 8: *Rumex dentatus* (n = 1), 9: *Oxalis corniculata* (n = 1), 10: *Sonchus asper* (n = 1), 11: *Syzygium species* (n = 1), 12: *Paspalum paspalodes* (n = 1), 13: *Heliotropium indicum* (n = 1), 14: *Ipomoea aquatica* (n = 5), 15: *Nelumbo nucifera* (n = 6), 16: *Eleocharis dulcis* (n = 4), 17: *Paspalum distichum* (n = 1), 18: *Paspalidium flavidum* (n = 3), 19: *Ludwigia adscendens* (n = 1), 20: *Ceratophyllum demersum* (n = 3), 21: *Paspalum* species (n = 1), 22: *Cyperus* species (n = 2), [b]AGPB/APB: Above ground plant biomass for EWSZ: Exposed wetland soil zone and APB: Aquatic plant biomass for SWZ: Shallow water zone and DWZ: Deep water zone, [c]g Dw m^{-2}: Grams of dry weight per meter square, [d]Mean values±standard error, [n]Sample size for each plant species

both NO_3^- and SO_4^{2-} for all the wetland zones at both the sites are well below the moderately inhibitory range (50 mg L^{-1} for NO_3^- and 500 mg L^{-1} for SO_4^{2-}) for methanogenic bacteria (Mittal, 1996) (Fig. 4a, 5b, 6, 7). Accordingly, spatial and temporal analysis were not conducted for NO_3^- and SO_4^{2-} as their content would only affect the CH_4 emissions considerably when NO_3^- and SO_4^{2-} concentrations exceed the inhibitory values for methanogenic bacteria.

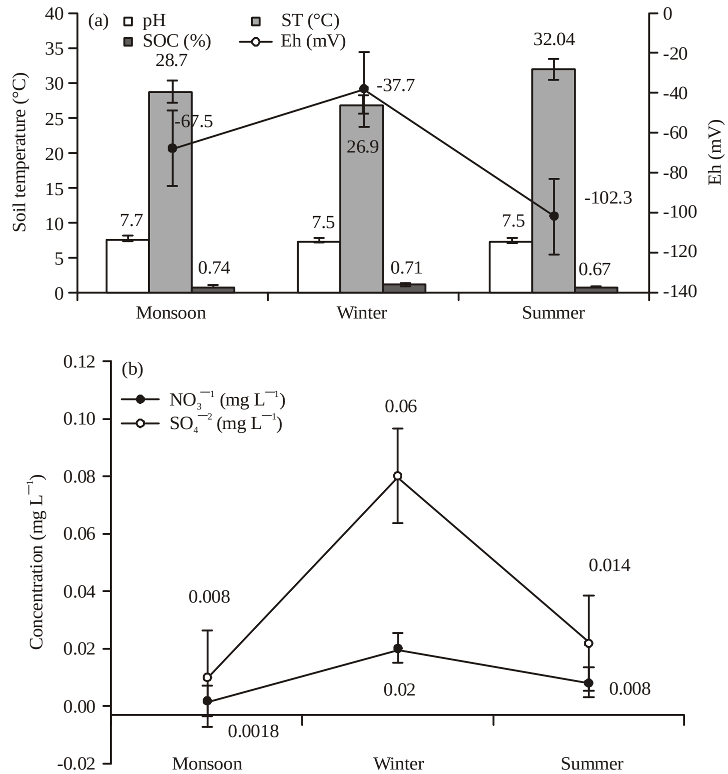


Fig. 5(a-b): Soil characteristics of Nawabganj Lake, Unnao (a) Seasonal variability in soil pH, Soil Temperature (ST), Soil Organic Carbon (SOC) and soil redox potential (Eh) to justify the seasonal CH_4 flux variations and (b) Nitrate (NO_3^-) and sulfate (SO_4^{2-}) contents in all the seasons were well below the moderately inhibitory range of 50 mg L^{-1} for NO_3^- and 500 mg L^{-1} for SO_4^{2-} for methanogenic bacteria

Water quality and CH_4 flux: Physical and chemical characteristics of water for both the sites are represented in Fig. 6 and 7. Water quality analysis deciphered that most part of the Nawabganj lake was shallow and static with low WD leading to low DO and high BOD. In contrast, Keetham lake was a flowing water system consisting of both shallow and stratified deep areas with high Dissolved Oxygen (DO) and low Biological Oxygen Demand (BOD) due to well mixed oxygenated conditions at high Water Depth (WD). Results showed that methanogenesis is supported by low DO levels, creating anoxic conditions and high BOD values indicating high microbial activity. The DO showed negative correlation and BOD showed positive correlation with CH_4 emissions (r = -0.74; p<0.01 in SWZ and r = -0.79; p<0.01 in DWZ for DO; r = 0.71; p<0.01 in SWZ and r = 0.77; p<0.01 in DWZ for BOD). Thus, for SWZ, CH_4 flux at Nawabgnaj lake with DO level of 4.8 mg L^{-1} and BOD level of 35.5 mg L^{-1} was higher as compared to Keetham lake with DO level of 6.3 mg L^{-1} and BOD level of 17.6 mg L^{-1}. Similarly, in DWZ, CH_4 flux at DO level of 2.1 mg L^{-1} and BOD level of 33.9 mg L^{-1} was higher for Nawabganj lake as compared to the CH_4 flux at DO level of 5.1 mg L^{-1} and BOD level of 21.2 mg L^{-1} in Keetham lake. Seasonally, the summer seasons showed high BOD and low DO values as compared to monsoon season and winter season at both the sites leading to maximum CH_4 flux during summer season at both the sites.

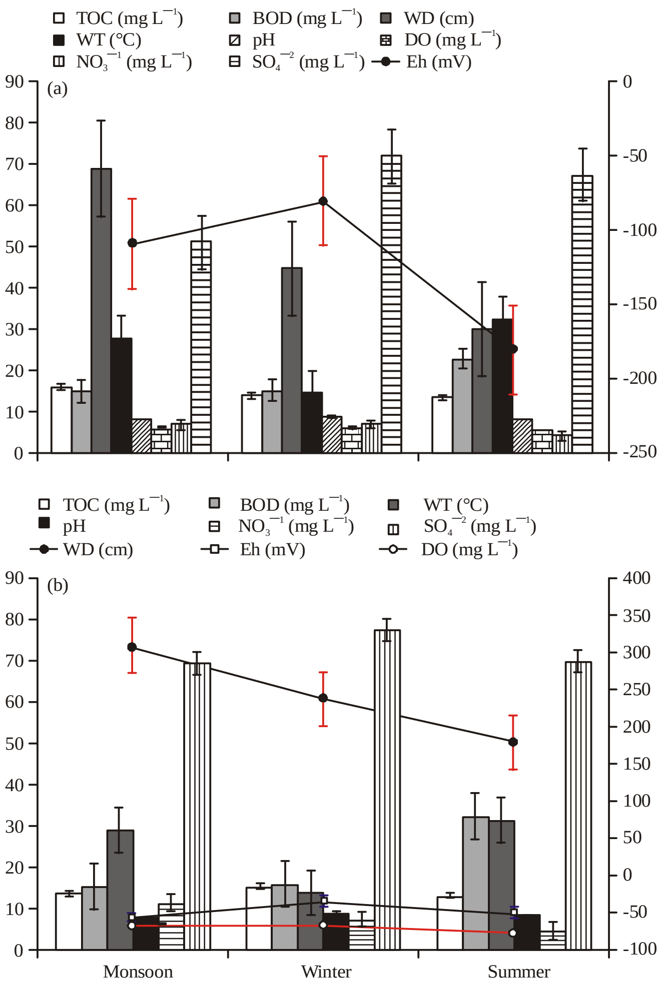


Fig. 6(a-b): Temporal variations in various water quality variables observed at Keetham Lake, Agra including Total Organic Carbon (TOC), Biological Oxygen Demand (BOD), Water Depth (WD), Water Temperature (WT), Water pH, Dissolved Oxygen (DO), nitrate (NO_3^-), sulfate (SO_4^{2-}) and water redox potential (Eh) to validate that seasonal CH_4 emissions for (a) Shallow Water Zone (SWZ) and (b) Deep Water Zone (DWZ)

In concordance with the outcomes reported by Bartlett and Harriss (1993), WD showed significantly negative correlation ($r = -0.73$; $p<0.01$ in SWZ and $r = -0.84$; $p<0.01$ in DWZ) with CH_4 emissions at both the sites indicating increased WD restricts the CH_4 generation and transport. Annual mean CH_4 flux for both zones in Nawabganj lake was found to be higher as compared to Keetham lake as annual averaged WD for SWZ (43.6 cm) and DWZ (140.6 cm) for Nawabganj lake was less than the annual averaged WD for both the zones in Keetham lake (50.2 cm for SWZ and 243.5 cm for DWZ). Considering CH_4 flux values for different seasons, CH_4 flux was found to be maximum in summer season as the WD dropped down to minimum in summer season to 30.2 and 15.2 cm (SWZ; at Keetham lake and Nawabganj lake), 180.3 and 45.2 cm (DWZ; at Keetham lake and Nawabganj lake) in comparison to monsoon season and winter season (Fig. 6, 7).

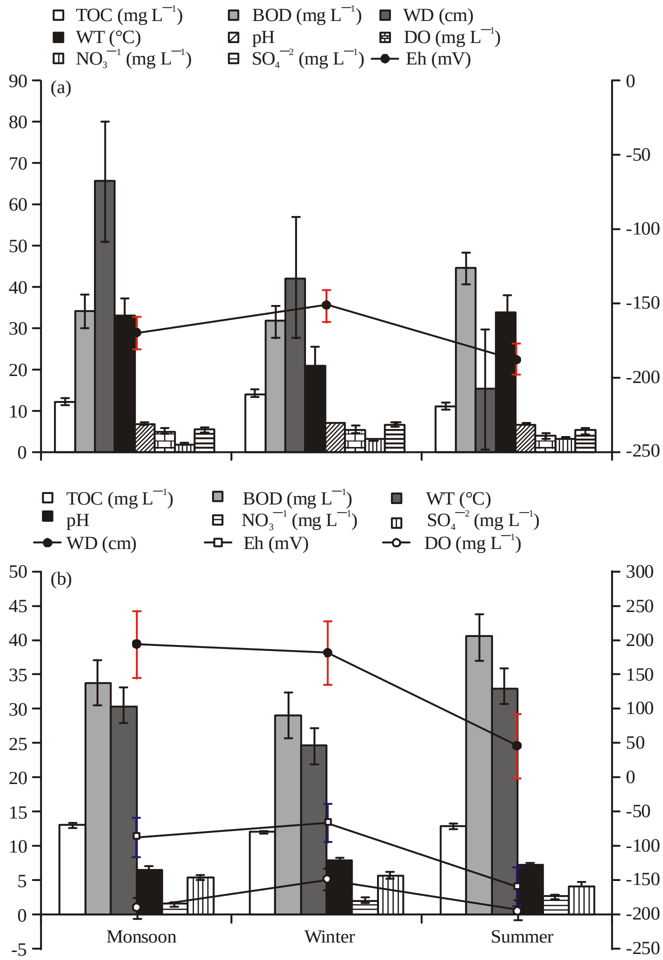


Fig. 7(a-b): Temporal variations in various water quality variables observed at Nawabganj Lake, Unnao including Total Organic Carbon (TOC), Biological Oxygen Demand (BOD), Water Depth (WD), Water Temperature (WT), Water pH, Dissolved Oxygen (DO), nitrate (NO_3^-), sulfate (SO_4^{2-}) and water redox potential (Eh) to validate the seasonal CH_4 emissions for (a) Shallow Water Zone (SWZ) and (b) Deep Water Zone (DWZ)

Total Organic Carbon (TOC) is another important CH_4 emission controlling variable in wetlands. Results revealed that TOC values at both the study sites were above the value (Fig. 6, 7) prescribed for a eutrophic lake i.e., 12.0 mg L^{-1} (Wetzel, 2001). TOC is not only the function of allochthonous organic matter contributed by inlet river and runoff from surrounding terrestrial environment but also depends upon autochthonous autotrophic production inside the lake. Spatially, though the Keetham lake exhibited slightly high TOC values (14.8 mg L^{-1}) than Nawabganj lake (12.3 mg L^{-1}) for SWZ, it displayed low CH_4 flux as the impact of TOC on CH_4 flux was counteracted by high DO, high WD and low BOD values observed at Keetham lake. It indicates that the methanogenesis was limited by the absence of suitable conditions of DO, BOD and WD even though the sufficient organic matter was available at Keetham lake for SWZ. Consequently, TOC showed negative correlation ($r = -0.61$; $p<0.01$) with CH_4 flux for SWZ. In case of DWZ, negative but comparatively weak correlation ($r = -0.42$; $p<0.05$) was observed between TOC and CH_4 as the TOC content was nearly the same at both sites, i.e., 13.9 mg L^{-1} for DWZ at Keetham lake and 12.8 mg L^{-1} for DWZ at Nawabganj lake.

Methanogenesis is a high pH sensitive process and a minor change in pH value markedly lowers the CH_4 emissions as the optimum pH range for CH_4 production was reported between 5.9-9.2 (Buchanan and Gibbons, 1975; Banik *et al.*, 1993). The pH was found to be negatively correlated with CH_4 emissions at both the sites for SWZ ($r = -0.50$; $p<0.01$) and DWZ ($r = -0.63$; $p<0.01$). It was observed that CH_4 emission increased as the pH decreased towards the neutral level of 6-7 and CH_4 emission would decline as it increased towards the maximum level of 9.2, as most of the methanogens are neutrophilic. With respect to spatial variations, pH values of Nawabganj lake were more favorable for methanogenesis as compared to those of Keetham lake resulting in higher mean annual CH_4 flux from Nawabganj lake. Temporally, no significant difference was noticed in pH and TOC values and hence no correlation analysis was performed for pH and TOC with CH_4 flux (Fig. 6, 7).

Redox potential (Eh) showed significant negative correlations ($r = -0.58$; $p<0.01$ for SWZ and $r = -0.93$; $p<0.01$ for DWZ) with CH_4 emissions. Thus, the decrease in Eh will result in more reduced conditions and hence enhanced CH_4 flux. Consequently, Nawabganj lake exhibited higher CH_4 flux due to more reduced conditions with low Eh values for SWZ (ranging from -187.8 to -151.6 mV with annual mean value of -172.0 mV±3.2; n = 18) and DWZ (ranging from -159.7 to -66.6 mV with annual mean value of -106.5±9.3 mV; n = 18) as compared to Keetham lake with high Eh values (ranging from -180.2 to -80.2 mV with annual mean value of -121.6±9.2 mV; n = 20 for SWZ and ranging from -58.9 to -35.6 mV with annual mean value of -48.4±2.9 mV; n = 12 for DWZ). Regarding temporal variability, lowest Eh values were found in summer season for the water zones at both the study sites with maximum CH_4 flux in comparison to monsoon and winter season (Fig. 6, 7).

Temperature governs the CH_4 production mainly through its effect on the activity of methanogens. The CH_4 production and emission increases with the increase in temperature and maximum CH_4 emission rates occur between 25 and 35°C (Wassmann *et al.*, 1998; Dubey, 2005). Analogous results have also been observed in the present study as the Water Temperature (WT) showed a positive correlation with CH_4 flux ($r = 0.51$; $p<0.01$ for SWZ and $r = 0.60$; $p<0.01$ for DWZ) at both the sampling sites. Eventually, SWZ and DWZ in Nawabganj lake showed greater CH_4 flux with higher annual averaged WT values of about 30.7°C for SWZ and 29.3°C at DWZ than Keetham lake where annual averaged WT values varied from 25.5°C at SWZ and 24.7°C at DWZ. With respect to seasonality, WT was found to be maximum during summers (32.8°C for SWZ and 31.3°C for DWZ in Keetham lake; 34.0°C for SWZ and 33.2°C for DWZ in Nawabganj lake) supporting high CH_4 flux and least during winters supporting least CH_4 flux (Fig. 6, 7).

Aquatic Plant Biomass (APB) and CH_4 flux: Aquatic vegetation (especially emergent vegetation) regulates the CH_4 emission primarily in two ways; firstly, by providing easily degradable organic substrates through plant biomass; secondly, by acting as conduits allowing CH_4 to escape out of the system through vascular transport from rhizosphere to atmosphere (Van Der Nat and Middelburg, 1998). Floral composition analysis indicated that the Nawabganj lake exhibited high annual averaged plant biomass for all the zones as compared to Keetham lake because Nawabganj lake was occupied by more diverse and dense aquatic vegetation throughout the lake, including *Eleocharis dulcis*, *Nelumbo nucifera*, *Ipomoea aquatica*, *Ceratophyllum demersum*, *Oplismenus burmannii*, *Ageratum conyzoids*, *Paspalum distichum*, etc. (Table 4 and 5). In Keetham lake, most of lake area was occupied by open water and vegetation was only present along the lake periphery dominated by *Phyla nodiflora*, *Alternanthera paronychioides*, *Polygonum lanigerum*, *Alternanthera sessilis*, *Paspalum distichum* etc.

It was observed that spatially, DWZ at Keetham lake was completely devoid of aquatic vegetation whereas DWZ at Nawabganj lake was occupied by *Nelumbo nucifera* along with free floating vegetation, including *Ceratophyllum demersum* and other varied types of submerged vascular plant and algae. Aquatic Plant Biomass (APB) showed a strong positive correlation with CH_4 emissions for DWZ with $r = 0.81$; $p<0.01$ in Nawabganj lake. High CH_4 flux with annual averaged APB in Nawabganj lake (10.4±1.7 g DW m^{-2}) as compared to Keetham lake indicated that the vegetated water surface releases more CH_4 than non-vegetated water surface. Similar observation has also been reported by Singh *et al*. (2000) for Indian wetlands, including both man-made and natural wetlands.

With respect to seasonal variability, APB also showed positive correlation with CH_4 flux for DWZ at Nawabganj lake supporting the fact that the increased APB in summer season (12.7 g DW m^{-2}) as compared to monsoon season (11.2 g DW m^{-2}) and winter season (7.2 g DW m^{-2}) enhanced the CH_4 flux to 239.9±24.7 mg m^{-2} day^{-1} during summer season than 114.2±12.3 mg m^{-2} day^{-1} in monsoon season and 71.5±5.6 mg m^{-2} day^{-1} during winter season.

For SWZ, APB showed no significant correlation ($r = -0.12$; $p>0.05$) with CH_4 emissions as SWZ at both the locations was occupied by macrophytic vegetation having nearly the same annual averaged APB including 18.1±3.6 g DW m^{-2} in Nawabganj lake and 15.0±3.9 g DW m^{-2} in Keetham lake (Table 4 and 5). Higher CH_4 flux for SWZ at Nawabganj lake than Keetham lake is probably due to the difference in CH_4 transport capabilities of individual plant species. The SWZ at Nawabganj lake was occupied by more diverse and rich aquatic emergent vegetation leading to more effective CH_4 transport capabilities as compared to the macrophytic vegetation present in SWZ at Keetham lake.

No specific temporal trend of APB in relation to CH_4 emissions was observed for SWZ at both the locations as the fluctuating water levels in SWZ represented a great impact on APB seasonally. For instance, in Nawabganj lake, APB in summer season was nearly close to that of winter season due to reduced growth of *Eleocharis dulcis* and *Ipomoea aquatica* in absence of sufficient standing water during summers. It was consistent with the results reported by Ding *et al*. (2002) according to which standing WD determines the vegetation distribution and governs the amount of plants litter inundated in the standing water which provides the substrates to methanogens for CH_4 production.

CONCLUSION

Present research highlights that temperature (WT and ST), Eh, WD, DO, BOD and plant biomass are the key predictors of seasonal CH_4 emissions, because these variables showed significant seasonal trend with respect to temporal variations in CH_4 emissions. Thus, temporal analysis showed highest CH_4 flux during summer season followed by monsoon season and least during the winter season due to more favorable conditions of above mentioned prime drivers of seasonal CH_4 flux. Present work also shows that different water regime zones and surrounding vegetation/soil contribute differently to CH_4 emissions from a wetland. Shallow Water Zone (SWZ) was the main contributor to CH_4 flux at both sites as CH_4 flux variability among different zones, varied as SWZ>DWZ>EWSZ at Nawabganj lake and SWZ>EWSZ>DWZ at Keetham lake. Accordingly, wetland zonation is required to be factored in estimating the CH_4 flux emitted from a wetland, to get more accurate and consistent results.

This study also demonstrates that a deep, flowing sparsely vegetated wetland (Keetham lake) exhibits lower CH_4 emission potential than the shallow, static densely vegetated wetland (Nawabganj lake) mainly due to the prevalence of well mixed oxygenated oligotrophic conditions at high WD and low contribution by autochthonous autotrophic production of aquatic vegetation. Thus, though the Keetham lake receives high anthropogenic carbon loadings from Yamuna and Hindon river via Agra canal, it represented a weak CH_4 emission source.

This study unveils that the despite of high organic and nutrient loadings, CH_4 emission potential of a wetland can be minimized by maintaining the appropriate water depth and checking the growth of highly proliferating aquatic weeds. Further, this will not only help to reduce CH_4 emissions but will also assist to control eutrophication and to maintain a lake in healthy condition. Therefore, in future, the CH_4 emission estimation should be the prime target of wetland management authorities. Finally, CH_4 emission data for Keetham lake and Nawabganj lake can be further utilized in preparing CH_4 emission budgets for other inland wetlands in tropical and subtropical regions or countries which may contribute to develop more effective wetland management strategies at regional and global scale.

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