Reviews and syntheses: Methane biogeochemistry in Sundarbans mangrove ecosystem, NE coast of India; a box modeling approach

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Abstract:

Biogeochemical cycling of CH₄ was studied in Sundarbans mangrove system during June 2010 to December 2012. The sediment was CH₄ supersaturated with mean production potential of 3547 & 48.88 µmol m⁻³ d⁻¹, respectively in case of intertidal (0 – 25 cm depth) & sub-tidal sediments (first 5 cm depth). This induces significant CH₄ out-flux from sediment to estuary via advective and diffusive transports. Mean advective (from intertidal sediment) and diffusive (from sub-tidal sediment) CH₄ fluxes were 159.52 µmol m⁻² d⁻¹ and 8.45 µmol m⁻² d⁻¹, respectively. Intertidal sediment CH₄ emission rate was about 4 times higher than surface layer CH₄ oxidation rate; indicating petite methanotrophic activity in mangrove sediment. Mean CH₄ concentration in estuarine surface and bottom waters were
69.90 and 56.17 nM, respectively. CH$_4$ oxidation in estuarine water column being 14 times higher than water - atmosphere exchange is considered as principal CH$_4$ removal mechanism in this estuary. Mean CH$_4$ mixing ratio over the mangrove forest atmosphere was 2.013 ppmv. The ecosystem acts a source of CH$_4$ to the upper atmosphere having mean biosphere - atmosphere exchange flux of 0.086 mg m$^{-2}$ d$^{-1}$. Mean CH$_4$ photo-oxidation rate in the mangrove forest atmosphere was 3.25 x 10$^{-9}$ mg cm$^{-3}$ d$^{-1}$ and is considered as principal CH$_4$ removal mechanism in the forest atmosphere. Finally, a box model presenting CH$_4$ biogeochemistry in Sundarbans biosphere reserve has been drafted and was used to demonstrate CH$_4$ budget in this ecosystem.

Keywords: methane, biogeochemistry, budget, mangrove, Sundarbans, India.

1. Introduction:

Methane (CH$_4$) is the key gaseous constituent of global carbon biogeochemical cycle in anaerobic environment. In carbon biogeochemical cycle, quantitatively 1% of the CO$_2$ fixed annually by photosynthesis is converted back to CO$_2$ by microorganisms via CH$_4$; the amount of CH$_4$ annually cycled in this way is around 1 billion tones (Rudolf et al. 2006). The atmospheric CH$_4$ mixing ratio increased from 0.72 ppbv in 1750 to 1.77 ppbv in 2005 (IPCC, 2007); creating a potential threat towards earth’s climate as CH$_4$ global warming potential is 26 times higher than CO$_2$ (Lelieveld et al. 1993). The cause of this large augmentation is not fully understood, but it is probably related to a surge
In CH$_4$ emission from wetlands that contributes approximately 20 - 39% of the annual global CH$_4$ budget (Hoehler et al. 2014).

Presenting accurate wetland CH$_4$ budget is very important for projecting the future climate. But, the primary problems in attempting to develop accurate CH$_4$ budget is the large spatial and temporal (Ding et al. 2003) variability in CH$_4$ emissions that reported all over the world. Being an integrated part of coastal wetlands, mangroves are relatively very less studied ecosystem with respect to CH$_4$ biogeochemistry (Barnes et al. 2006; Biswas et al. 2007; Bouillon et al. 2007c; Kristensen et al. 2008).

Consequently, presenting wider CH$_4$ and carbon budgets for mangrove ecosystem globally is problematic.

Mangroves are one of the most productive coastal ecosystems and are characterized by high turnover rates of organic matter, both in the water column and in sediment. The organic matter mineralization in sediment is a multi-step process, which begins with an enzymatic hydrolysis of polymeric material to soluble monomeric and oligomeric compounds. Under oxic conditions the organic carbon (OC) is directly mineralized to carbon dioxide and water. But, the mangrove sediments are rich in clay content that reduces the porosity of the sediment and helps in the formation and retention of anoxic condition (Dutta et al. 2013). OC mineralization in anaerobic environment is typically complex involving various microbes in initial de-polymerization followed by fermentative microbial break down of complex organic compounds to small moieties. The end products of the fermentation process used by methanogens in the final step of anaerobic decomposition can also be used by microbial groups that
utilize a variety of inorganic terminal electron acceptors (TEAs) in their metabolism (Megonigal et al. 2004). The competitiveness, and thus relative importance, of these TEAs is thought to be controlled primarily by their thermodynamic favourability in the following order: NO$_3^-$ (denitrification), Fe (III) (iron reduction), Mn (III, IV) (manganese reduction), and SO$_4^{2-}$ (sulphate reduction) (Keller et al., 2013).

Methanogenesis remains suppressed by more favourable TEA-reducing processes and begins when all those TEAs have been consumed and electron donors are in surplus. In fact CH$_4$ is produced by fermentative disproportionation reaction of low molecular compounds (e.g. acetate) or reduction of CO$_2$ by hydrogen or simple alcohols (Canfield et al. 2005) depending upon redox condition of sediment, which is reported to be ≤ 150 mV for the process of methanogenesis (Wang et al. 1993). The sedimentary produced CH$_4$ partially escapes through diffusion and direct ebullition to the atmosphere after partially being oxidized at surface (aerobic oxidation) and subsurface sediments (anaerobic oxidation), while the remaining dissolves in pore water resulting super-saturation. During low tide condition, the CH$_4$ rich pore water transports to the adjacent creeks and estuaries depending upon hypsometric gradient. In addition, CH$_4$ produced in the underlying sediment of the estuary (sub-tidal sediment) diffuses upward to further enrich the dissolved CH$_4$ level in estuarine water column.

In the estuarine water column, the supplied CH$_4$ is partly oxidized to CO$_2$ by methanotrophs, which use CH$_4$ as the sole carbon source (Hanson and Hanson, 1996). Aerobic CH$_4$ oxidation in the aquatic systems significantly reduces the CH$_4$ flux across water – atmosphere interface. In case of stratified systems like lakes, pelagic CH$_4$ oxidation can consume up to 90 % of the dissolved CH$_4$ (Utsumi et al. 2004).
1998a; Kankaala et al. 2006), whereas in the well-mixed estuaries, CH$_4$ oxidation is believed to be much less efficient (Abril et al. 2007). The CH$_4$ that escapes from microbial oxidation partially emits from estuary across water - atmosphere interface and remaining exports to adjacent continental shelves region.

The emitted CH$_4$ from sediment – atmosphere and water – atmosphere interfaces of the mangrove ecosystem enrich the atmospheric CH$_4$ mixing ratio at a regional level (Mukhopadhyay et al. 2002) and further participates in complex atmospheric CH$_4$ cycle. In the mangrove forest environment, emitted CH$_4$ partially exchanges across biosphere - atmosphere interface depending upon micrometeorological conditions; while the major fraction undergoes photo-oxidation depending upon ambient NO$_x$ level. A schematic diagram of atmospheric CH$_4$ photo-oxidation with/without NO$_x$ concentration is presented in Fig.1 (modified from Wayne, 1991).

This study aimed to report production, oxidation, distribution and fluxes of CH$_4$ in different sub-ecosystems of Sundarbans for complete understanding of CH$_4$ biogeochemistry in the estuarine mangrove environment. Beyond this primary objective, another main objective of this study was to demonstrate a comprehensive CH$_4$ budget for Sundarbans biosphere reserve.

2. Study location:

Sundarbans is the largest single block of tidal mangrove forest in the world, situated over India and Bangladesh at the land ocean boundary of Ganges-Brahmaputra delta and the Bay of Bengal. This
extensive natural mangrove forest was inscribed as a UNESCO world heritage site and covers an area of 10,200 sq. km of which 4200 sq. km of reserved forest is spread over India and rest part is in Bangladesh. The Indian Sundarbans Biosphere Reserve (SBR) is extended over an area of 9600 km² constituted of 1800 sq km estuarine waterways and 3600 sq. km reclaimed areas along with above stated mangrove reserve forest. The forest is about 140 km in length from east to west and extends approximately 50 – 70 km from the southern margin of the Bay of Bengal towards the north. The Indian part of the Sundarbans mangrove delta is crisscrossed by the estuarine phases of several rivers namely Mooriganga, Saptamukhi, Thakuran, Matla, Bidya, Gosaba and Haribhanga forming a sprawling archipelago of 102 islands out of which 54 are reclaimed for human settlement and rest are virgin. One of these virgin Islands is the Lothian Island, which is situated at the buffer zone of the Sundarbans Biosphere Reserve covering an area of 38 km². This island completely intertidal and occupied by thick, robust and resilient mangroves trees with a mean height of < 10 m. Among the mangroves, *Avicennia alba*, *Avicennia marina* and *Avicennia officinalis* are the dominant species, *Excoecaria agallocha* and *Heritiera fomes* are thinly distributed and *Ceriops decandra* is found scattered all over the island. The mangrove sediment is silty clay in nature and composed of quartzo-feldspathic minerals like quartz, albite and microline. The adjacent estuarine system of the island is Saptamukhi which has no perennial source of freshwater and receives significant amounts of agricultural and anthropogenic runoff especially during monsoon. Climate in the study area is characterized by premonsoon (February – May), south west monsoon (June – September) and north east monsoon or postmonsoon (October –
January). Based on the above the Lothian Island and associated Saptamukhi estuary have been chosen for studying CH$_4$ biogeochemical cycle in the Sundarbans mangrove environment. A location map of Sundarbans showing Lothian Island and Saptamukhi estuary in the subset is presented in Fig.2.

3. Materials and methods:

The present study was carried out during June 2010 to December 2012 to cover the seasonal variation in the study area. Sediment and atmospheric samples were collected from the intertidal mangrove sediment & watch tower located in the center of the Lothian Island (21° 42.58’N: 88°18’E), respectively. Moreover, water samples were collected from the estuarine mixing zones of the Saptamukhi estuary. The details of study design, analyzed parameters and flux calculations are described in the following sections.

Intertidal sediment samples were collected at different locations of the mangrove forest covering upper, mid and lower littoral zones with the help of stainless steel corers (diameter: 10 cm) with an mean penetration depth of 25 cm. Sediment cores were sectioned at 5 cm interval and collected in zipper bags for transporting to the laboratory. Surface sediment temperature was measured in-situ using thermometer. Simultaneously estuarine bottom sediment (sub-tidal) was also collected using grab samplers. CH$_4$ production was measured by anaerobic incubations of sediment samples. A small portion of sample (about 10 g) were weighed and taken in an incubation bottle (1.2 cm i.d. and 10 cm long) fitted with rubber septum. Then the bottles were flushed with pure N$_2$ for 1 min to create a completely
anaerobic condition. The incubation was carried out in duplicate at ambient temperature for 24 hrs. At
the end of incubation 1 ml gas sample was withdrawn from the headspace through the rubber stopper
using a gas-tight glass syringe (Lu et al. 1999). CH$_4$ accumulation in the headspace was determined by
gas chromatography (Varian CP3800 GC) fitted with chrompack capillary column (12.5 m x 0.53 mm)
and a flame ionization detector (FID) having a mean relative uncertainty of ± 2.9 % with reference to
the purity of nitrogen for CH$_4$ as blank. CH$_4$ production was calculated according to CH$_4$ accumulation
in the headspace, the headspace volume and volume of samples.

Wet sediment samples (both intertidal and sub-tidal) are processed for measurement of CH$_4$
concentration according to Knab et al. 2009 followed by measurement of headspace for CH$_4$ by gas
chromatography as described above. The nitrate, nitrite and ammonia concentrations of the sediment
samples were measured taking 2M KCl extract of sediment followed by standard spectrophotometric
method (Grasshoff 1983). CH$_4$ oxidation was measured for intertidal surface sediment only, following
incubation with CH$_4$ spiked air. A fixed volume of surface sediment (~6 ml) was taken in 60 ml flasks
fitted with rubber septum and head space air (21% O$_2$) was spiked with 100 µL CH$_4$ L$^{-1}$ (10 ppmv CH$_4$
procured from Chemtron Science Laboratories Pvt. Ltd.). These flasks were incubated in duplicate at
ambient temperature for 4 days. Gas samples from the head-space was drawn immediately at the onset
of incubation and at 24 hours interval till the end for analyzing CH$_4$ concentration using gas
chromatograph as described earlier. CH$_4$ oxidation was calculated according to decrease of CH$_4$
concentration in the headspace, the headspace volume and volume of sediment samples.
During low tide condition CH$_4$ emission from the intertidal sediment surface to the atmosphere was measured using static Perspex chamber method (Purvaja et al. 2004). The chambers were placed in the sediment for a particular duration and CH$_4$ emission rate was calculated based on the enrichment of CH$_4$ mixing ratio inside the chamber in comparison to the ambient air. Mixing ratio of CH$_4$ was measured by gas chromatography as described earlier. Advective CH$_4$ fluxes from intertidal forest sediment to the estuarine water column ($F_{ISW}$) were computed as (Reay et al. 1995): $F_{ISW} = \Phi \times v \times C$; where, $\Phi =$ porosity of sediment = 0.58 (Dutta et al. 2013), $v =$ mean linear velocity = $d\Phi^{-1}$ (d = specific discharge), $C =$ pore water CH$_4$ concentration in intertidal sediment. The specific discharge for the intertidal sediment was recorded by measuring the rate of accumulation of pore water in an excavated pit of known surface area (Dutta et al. 2015b). This was done during low tide condition in the intertidal flat at 100 m intervals along with receding water level. Diffusive CH$_4$ flux from sub-tidal sediment to estuary was calculated using Fick’s law of diffusion (Sansone et al. 2004).

Collection and analysis of dissolved CH$_4$ concentration using gas chromatograph for estuarine water has been described elsewhere (Dutta et al. 2013). For measurement of CH$_4$ oxidation water was filled in pre-cleaned (acid washed and sterilized) septum fitted incubation bottles (in a batch of 12 bottles) from Niskin samplers with gentle overflowing and sealed with no air bubbles. Immediately after collection two bottles are poisoned with HgCl$_2$ to stop microbial CH$_4$ oxidation and they are considered as control for the experiment. Rest of the bottles are kept for incubation in ambient condition with two bottles withdrawn from incubation daily and were poisoned with saturated HgCl$_2$ solution to continue the
incubation experiment up to a times series of 5 days. The concentrations of dissolved \( \text{CH}_4 \) in all incubated samples was measured to record a time series kinetics of \( \text{CH}_4 \) oxidation. From the time series plot, the specific rate of \( \text{CH}_4 \) oxidation was calculated by linear regression of the natural log of \( \text{CH}_4 \) concentration against time. The value of specific rate of \( \text{CH}_4 \) oxidation is equivalent to the slope of the regression line. Actual rates of \( \text{CH}_4 \) oxidation (\( \text{CH}_4 \) consumption rate) were calculated by the product of dissolved \( \text{CH}_4 \) concentration and specific rate of \( \text{CH}_4 \) oxidation (Utsumi et al. 1998b).

\( \text{CH}_4 \) flux across the air - water interface was calculated according to the expression (Liss and Merlivat 1986): \( F_{WA} = k \Delta C \); where, \( \Delta C \) is the difference in concentrations ([\( \text{CH}_4 \)\text{observed} ] - [\( \text{CH}_4 \)\text{equilibrium}]) and \( k \) is the gas transfer velocity in cm hr\(^{-1}\) was calculated from wind velocity and schmidt number (Liss and Merlivat 1986). A positive value denotes flux from water to the atmosphere and vice versa. Water temperature and pH were recorded in situ using a thermometer and a portable pH meter (Orion Star A211) with a Ross combination electrode calibrated on the NBS (US National Bureau of Standards) scale (Frankignoulle and Borges 2001). Reproducibility was ± 0.005 pH units. Transparency of the water column was measured with a 15 cm diameter Secchi disc. Salinity and dissolved oxygen concentrations in surface and bottom waters were measured onboard, following the Mohr-Knudsen and Winkler titration methods, respectively (Grasshoff et al. 1983). For estimating of nitrite, nitrate and ammonia concentrations samples were collected in 1L HDPE bottles and stored on ice during transportation to the laboratory. In the laboratory concentrations were measured using standard spectrophotometric method (Grasshoff et al. 1983) and the values were added to compute dissolved
inorganic nitrogen concentration (DIN). For estimating of chlorophyll concentrations samples were collected in 1L amber colored bottles and stored on ice during transportation to the laboratory. In the laboratory chlorophyll concentration was measured using a standard spectrophotometric method (Parsons et al. 1992). Primary productivity and community respiration in the estuarine surface water were measured in situ by a light and dark bottle oxygen method (Parsons et al. 1992) with a relative uncertainty of ± 2.5%.

Samples for measurement of CH$_4$ mixing ratio were collected in air sampling bulbs from both 10 m and 20 m heights and transported to laboratory for analysis. Samples were analyzed using gas chromatography (Varian CP 3800GC) fitted with chrompack capillary column (12.5 m x 0.53 mm) and a flame ionization detector (FID). Two reference gas standards (10.9 ppmv and 5 ppmv, supplied by Chemtron Science Laboratories Pvt. Ltd) were used before and after every measurement. Duplicate samples were analyzed periodically and the replicate measurements were found to be within 2 - 3.2%.

Meteorological parameters like air temperature and wind velocity were simultaneously recorded at 10 and 20 m heights using a portable weather monitor (Model: Davis 7440) and the value was used to calculated micrometeorological indices like friction velocity ($U^*$), roughness height ($Z_o$), drag coefficient and planetary boundary layer height (Ganguly et al. 2008). Biosphere - atmosphere CH$_4$ exchange flux ($F_{BA}$) was calculated using the following relation (Barrett 1998; Ganguly et al. 2008):

$$F_{BA} = V_C \Delta \chi.$$

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Where, $\Delta \chi =$ difference of mixing ratio of CH$_4$ between 10 and 20 m height. $V_C =$ exchange velocity which is defined as $1 / (r_a + r_s)$ ($r_a =$ aerodynamic resistance and $r_s =$ surface layer resistance). Negative flux indicates net transfer from the atmosphere to the biosphere and positive flux indicates emission.

CH$_4$ photo-oxidation rate (P) in the lower mangrove forest atmosphere was calculated based on the reaction (CH$_4$ + OH $\rightarrow$ CH$_3$ + H$_2$O) as: $P = k [\text{CH}_4] [\text{OH}]$; where, $k =$ rate constant of the reaction between CH$_4$ and OH $= 1.59 \times 10^{-20} T^{-2.84} \exp (-978 / T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Vaghjiani and Ravishankara 1991). [CH$_4$] $=$ mean of all CH$_4$ mixing ratio measurements during the day time at 10 m height in the diurnal cycle and [OH] $=$ mean of all OH radical concentrations during the day time at 10 m height in the diurnal cycle in molecules cm$^{-3}$. OH radical concentration was computed using photolysis frequency of O$_3$ based on the empirical relation proposed by Ehhalt and Rohrer, 2000.

4. Results and discussion:

4.1 CH$_4$ cycling in the mangrove sediment:

Mean CH$_4$ production potential of 20 - 25 cm deep sediment layer of the mangrove forest was 5831 µmol m$^{-3}$ d$^{-1}$ which is about 7.9 times higher than production potential measured for 5 – 10 cm depth (table 1). Surface layer (0 – 5 cm) CH$_4$ production potential was not measured at the study point, considering diminutive methanogenic and immense methanotrophic activity in that layer. The profile could not cover up to the end of the methanogenic sediment layer, but the value clearly indicates enormous CH$_4$ production potential of the mangrove system with a mean of 3547 µmol m$^{-3}$ d$^{-1}$. The
production potentials measured for this tropical mangrove forest sediment were within the range of that reported for pristine mangrove forest at Balandra, Mexico (Strangmann et al. 2008). On seasonal basis, highest production potential (4616 ± 2666 µmol m⁻³ d⁻¹) was noticed during postmonsoon and lowest (2378 ± 1799 µmol m⁻³ d⁻¹) during premonsoon periods. The peak postmonsoon CH₄ production potential may be attributed to maximum mangrove litter fall (58.79 gm dry wt C m⁻² month⁻¹; Ray et al. 2011) mediated supply of organic matter in the inter-tidal sediment and subsequently inducing higher CH₄ production. In contrast, high premonsoon salinity regime of the ecosystem may partially inhibited CH₄ production potential of the system by supplying higher SO₄²⁻ and subsequent enhanced SO₄²⁻ reduction during this phase (Dutta et al. 2015b). Geochemistry of the mangrove sediment related to this study is briefly discussed elsewhere (Dutta et al. 2013) but a general trend is presented in Fig.3. The Fig.3A indicates in this inter-tidal mangrove sediment requisite redox condition for the process of methanogensis (<150 mV; Wang et al. 1993) is attained at ≈ 10 - 25 cm depth while the process of SO₄²⁻ reduction was prominent in the upper 20 cm sediment (Fig.3B). The decreasing trend of %OC across deep mangrove sediment indicates significant OC mineralization by anaerobic microbial metabolism (Fig.3C).

CH₄ production potential of first 5 cm deep sub-tidal sediment layer varied between 18.72 – 85.74 µmol m⁻³ d⁻¹ having maximal (77.06 ± 12.27 µmol m⁻³ d⁻¹) postmonsoon and minimal (21.28 ± 3.63 µmol m⁻³ d⁻¹) premonsoon. Mean methanogenesis rate of sub-tidal sediment (0 – 5 cm) was 48.88 ± 26.04 µmol m⁻³ d⁻¹. %OC of sub-tidal sediment surface ranged from 1.56 ± 0.72 to 2.21 ± 0.69 having maximum
concentration during postmonsoon and minimum during premonsoon period. About 35.25 % higher OC supply in sub-tidal surface layer during postmonsoon period compare to premonsoon might have caused strong redox condition favoring a higher rate of CH₄ production.

The %OC underwent anaerobic transformation in the 5 - 10, 10 - 15, 15 - 20 and 20 - 25 cm depths were 12.7%, 9.94%, 7.64% and 8.23%, respectively. Methanogens utilize a limited number of substrates and the major pathways are through fermentation of acetate (acetoclastic) and reduction of CO₂ with H₂ (hydrogenotrophic). The pathways for both types of methanogenesis are as follows:

\[
P - I = \text{Acetoclastic methanogenesis; } P - II = \text{Hydrogenotrophic methanogenesis}
\]

Among these two, in high CO₂ rich environment acetoclastic methanogenesis is predominant over hydrogenotrophic one and approximately 70% of biologically produced CH₄ originates from conversion of the methyl group of acetate to CH₄ (Mayumi et al. 2013). Based on the above fact in the intertidal mangrove sediment up to the depth of penetration 25 cm, acetoclastic methanogenesis mediated OC utilization rate was 59.58 mg m⁻³ d⁻¹ resulting 2483 µmol m⁻³ d⁻¹ of CH₄. The estuarine bottom sediment was also OC as well as CO₂ rich and 0.82 mg m⁻³ d⁻¹ of OC transformed through acetoclastic methanogenesis producing 34.22 µmol m⁻³ d⁻¹ of CH₄. Extrapolating the values for entire Sundarbans, it
is estimated that in the Sundarbans mangrove sediment (both inter and sub tidal sediments) about 22.86 Ggyr\(^{-1}\) of OC was transformed through methanogenic pathway resulting 15.25 Ggyr\(^{-1}\) of CH\(_4\). The mechanism also produces another radiatively active trace gas (CO\(_2\)) as a by-product of CH\(_4\) production & acetoclastic methanogenesis mediated CO\(_2\) production rate of this mangrove forest sediment was 109.23 mg m\(^{-3}\) d\(^{-1}\).

A major part of sedimentary produced CH\(_4\) dissolves in the pore water at in situ high pressure resulting significant super saturation (Dutta et al. 2013). Pore water CH\(_4\) concentrations along intertidal forest sediment depth profile are presented in table 1 indicating almost constant concentration up to 10 - 15 cm sediment layer which abruptly increase 1.79 times at 15 - 20 cm depth and further increase to 2.26 – 2.76 times at 20 - 25 cm depth. On annual basis intertidal sediment pore water CH\(_4\) concentrations ranged between 3204 ± 1325 to 3639 ± 1949 nM, being maximal postmonsoon and minimal premonsoon periods (Dutta et al., 2015b).

Statistical analysis (using MINITAB version 17) was performed between pore water CH\(_4\) concentration ([CH\(_4\)]\(_{PW}\)) vs. E\(_h\), NO\(_2^-\), SO\(_4^{2-}\), AVS and organic carbon percentage (%OC) in order to point out key controlling factor for variability of pore water CH\(_4\) concentration in intertidal sediment. Here the dependent variable is [CH\(_4\)]\(_{PW}\) and independent variables are E\(_h\), NO\(_2^-\), SO\(_4^{2-}\), AVS and % OC. The regression equation between dependent and independent variables are as follows: [CH\(_4\)]\(_{PW}\) = 10.6 - 0.0184 E\(_h\) - 0.123 NO\(_2^-\) - 0.0076 SO\(_4^{2-}\) - 0.0693 AVS - 4.09 %OC (R\(^2\) = 86.6%, F = 7.79, p = 0.004, n =
From the statistical analysis (table 2) it was found that \([\text{CH}_4]_{\text{PW}}\) was significantly correlated with 
\(\%\text{OC}\) (\(p = 0.004\)) and \(E_h\) (\(p = 0.013\)) of sediment, indicating cumulative influence of \(\%\text{OC}\) and \(E_h\) on
variability of \([\text{CH}_4]_{\text{PW}}\) in this tropical mangrove forest.

Following same seasonal trend annual mean pore water \(\text{CH}_4\) concentrations in estuarine bottom lying
sediment varied between 2770 ± 1039 to 3980 ± 1227 nM (Dutta et al., 2015b). Compare to the adjacent
estuarine water (will be discussed in section 4.2) sediment pore water was 53.4 times \(\text{CH}_4\)
supersaturated; induces significant \(\text{CH}_4\) influx from intertidal & sub-tidal sediment to estuary.
Advective \(\text{CH}_4\) fluxes from intertidal sediment to adjacent estuary were between 115.81 ± 31.02 and
199.15 ± 47.89 µmol m\(^{-2}\) d\(^{-1}\), having maximal postmonsoon and minimal premonsoon periods (Dutta et
al., 2015b) (Fig.4). The peak postmonsoon advective \(\text{CH}_4\) flux may be ascribed to higher pore water
\(\text{CH}_4\) concentration as well as specific discharge (0.008 cm min\(^{-1}\)). Diffusive \(\text{CH}_4\) fluxes from estuarine
bottom lying sediment to the water column ranged from 7.06 ± 1.95 to 10.26 ± 2.43 µmol m\(^{-2}\) d\(^{-1}\)
(Fig.4), having an annual mean of 8.45 µmol m\(^{-2}\) d\(^{-1}\) (Dutta et al., 2015b). The diffusive fluxes
calculated for this ecosystem were comparatively higher than Yantze estuary (1.7 – 2.2 µmol m\(^{-2}\) d\(^{-1}\)
(Zhang et al. 2008b) but much lower than White Oak river estuary (17.1 mmol m\(^{-2}\) d\(^{-1}\)) (Kelly et al.
1990). Fluxes were maximal during postmonsoon and minimal during pre-monsoon periods. The peak
postmonsoon diffusive \(\text{CH}_4\) fluxes may be ascribed to maximal pore water \(\text{CH}_4\) concentrations while the
reverse case applies premonsoon.
From the methanogenic deep sediment layer the produced CH$_4$ partially diffuses upward, which undergoes aerobic and anaerobic oxidation in sediment before being transported to the forest atmosphere. But only aerobic CH$_4$ oxidation at sediment surface has been included in this study. The seasonal variation of surface sediment CH$_4$ oxidation potentials are presented in Fig.5 and the values were within the range of that reported for deciduous forest of UK and temperate forests soil in Korea (Bradford et al. 2001b; Jang et al. 2006). On seasonal basis, the oxidation potential was maximal premonsoon and minimal monsoon periods having a mean of 1.758 ± 0.34 mg m$^{-2}$ d$^{-1}$. The peak premonsoon CH$_4$ oxidation potential may be due to maximum soil surface temperature (table 1) as methanotrophy is a microbiological process and rate of any microbiological reaction is directly proportional with temperature. NH$_4^+$ and NO$_3^-$ concentrations in mangrove forest sediment surface varied between 1.01 – 3.31 µM and 1.11 – 2.98 µM, respectively and correlation between NH$_4^+$ and NO$_3^-$ concentrations vs. CH$_4$ oxidation potential ([CH$_4$]$_{(Ox)}$ = 1.63 - 0.307 [NH$_4^+$] + 0.293 [NO$_3^-$] [$R^2 = 68 \%$, $F = 3.18$, $p = 0.181$, n = 15]) revealed negative relationship between [CH$_4$]$_{(Ox)}$ and [NH$_4^+$] but positive with [NO$_3^-$] (table 3). The inhibitory effect of [NH$_4^+$] on CH$_4$ oxidation activity may be due to competition of NH$_4^+$ with CH$_4$ for the CH$_4$ monooxygenases (MMO) in methanotrophic bacteria. Even though the affinity of MMO for CH$_4$ is 600 - to 1300 - fold higher than its affinity for ammonium, high concentrations of ammonium are known to substantially inhibit the process of methanotrophy in sediment (Be´dard and Knowles, 1989). Proportional relationship between NO$_3^-$ and CH$_4$ oxidation may be related to the demand of type II methanotrophic bacteria for nitrogen sources (Jang et al., 2006).
After oxidation the residual diffused CH$_4$ emits across sediment – atmosphere interface. Monthly variation of mangrove sediment – atmosphere CH$_4$ exchange fluxes are presented in Fig.6; having maximal emission during monsoon and minimal during premonsoon (Dutta et al. 2013). Emission fluxes estimated for this study point were within the range of that reported for Pichavarm mangrove, India and mangrove along the south west coast of Puerto Rico (Purvaja et al. 2004; Sotomayor et al. 1994). Mean soil CH$_4$ emission from this mangrove ecosystem was 7.06 mg m$^{-2}$ d$^{-1}$; indicates the mangrove sediment acts as a rich source of CH$_4$ to the regional atmosphere. During the observation period soil temperature (t) ranged between 18.25 ± 0.22 and 28.36 ±1.02$^\circ$C and variability of soil CH$_4$ emissions ($E_M$) were tested statistically with respective ‘t’ and pore water salinity (s). $E_M$ is best fitted linearly with ‘t’ and by a second order polynomial equation with ‘s’ as given below:

$$E_M = 0.066 t - 1.79 \ (R^2 = 0.35, F = 5.33, p = 0.041, n = 12)$$

$$E_M = 0.0039 s^2 -0.2006 s + 2.8416 \ (R^2 = 0.77, F = 7.71, p = 0.029, n = 12)$$

The analysis indicates significant correlation between CH$_4$ fluxes with both the independent variables, indicating cumulative influences of ‘t’ and ‘s’ on mangrove soil CH$_4$ emission. Similar phenomenon was previously reported in Ranong Province mangrove area, Thailand (Lekphet et al. 2005) and a salt marsh of Queen’s creek (Bartlett et al. 1987). Comparing CH$_4$ emissions from different littoral zones of the mangrove forest, higher emissions (0.288 - 0.507 mg m$^{-2}$ hr$^{-1}$) were noticed from upper littoral zone compare to mid & lower littoral zones; may be due to the higher pneumatophore density in that region (42 number m$^{-2}$) and diffusion of CH$_4$ through it (Dutta et al. 2013). Mean pneumatophore and
Bioturbation density in the forest area was counted as 45 ± 7 and 12 ± 2 nos. m⁻², respectively and statistical analysis was done in order to examine the influence of pneumatophore and bioturbation on emission of CH₄ in this mangrove forest atmosphere. Regression equations between soil CH₄ emission rate (F_SA) vs. pneumatophores (P_no) and bioturbation (B_no) density were as follows:

\[ F_{SA} = -8.59 + 0.330 \times P_{no} \quad (R^2 = 81.9\%, F = 6.94, p = 0.032, n = 20) \]

\[ F_{SA} = 6.42 - 0.052 \times B_{no} \quad (R^2 = 61.9\%, F = 5.94, p = 0.041, n = 20) \]

The statistical analysis revealed significant correlation between dependent & independent variables for both cases indicating other than physicochemical factors, biological variables (like presence of pneumatophore and bioturbation) also play a crucial role for CH₄ emission from the forest sediment. The positive correlation between sediment CH₄ emission rate and pneumatophore density indicates plant mediated emission of CH₄ in Sundarbans mangrove ecosystem whereas negative correlation with bioturbation density indicates that burrows favored sediment oxygenation especially in surface layer, resulting CH₄ oxidation in surface mangrove sediment and ultimately reduced its emission flux from sediment. A similar observation on oxidation of surface sediment by crab burrows in the mangrove environment was previously reported by Kristensen and Alongi, 2006.

**4.2 Estuarine CH₄ cycling:**
Physicochemical and biological parameters of the estuarine water column are presented in table – 4 and on monthly basis from Fig.7A to 7D. For both (temperature and salinity) the values were highest during the premonsoon and lowest during the postmonsoon (for temperature) and monsoon (for salinity) months. Marginal variation of temperature and salinity in estuarine surface and bottom water clearly indicates a vertically well mixed water column. Surface water pH varied over a narrow range (8.10 ± 0.03 to 8.17 ± 0.16) and seasonal differences were not significant. Dissolved oxygen (DO) concentrations in estuarine surface and bottom waters were high (6.04 ± 0.73 to 7.27 ± 1.14 mg L\textsuperscript{-1} and 5.41 ± 0.03 to 5.98 ± 0.79 mg L\textsuperscript{-1}, respectively) being maximal during postmonsoon and minimal during monsoon periods. DO % of saturation varied between 94.8 and 99.3; indicates a well oxygenated water column that would inhibit the anaerobic microbial metabolism of organic matter within estuarine water column. The chlorophyll concentration in estuarine surface water ranged from 3.11 ± 0.39 to 7.88 ± 1.90 µg L\textsuperscript{-1} having highest and lowest concentrations during postmonsoon and monsoon, respectively. Seasonal trends of chlorophyll concentration mirrored the changes in Secchi disc depth, which ranged between 29.7 ± 7.8 and 75.9 ± 7.7 cm during the study period. The ratio between primary productivity and community respiration was <1, indicates the estuary is net heterotrophic in nature.

During the observation period estuarine surface and bottom waters dissolved CH\textsubscript{4} concentrations ranged from 54.20 ± 5.06 to 90.91 ± 21.20 and 47.28 ± 12.85 to 67.97 ± 33.12 nM, respectively (Fig.7E); having maximal postmonsoon and minimal monsoon periods (table 4) (Dutta et al., 2015b). The CH\textsubscript{4} concentrations measured in this mangrove dominated estuary was within the range of that measured in
Thames estuary, Loire estuary but higher than Hooghly estuary, Yangtze River estuary, Sado estuary and Elbe estuary (Middelburg et al. 2002; Biswas et al. 2007; Zhang et al. 2008b). The peak postmonsoon CH$_4$ concentrations may be attributed to cumulative effect of maximal supply of dissolved CH$_4$ rich pore water from intertidal mangrove sediment and minimal CH$_4$ oxidation (will be discussed later) in the estuarine water column. Like other tropical, sub-tropical and temperate estuaries (Upstill-Goddard et al. 2000; Middelburg et al. 2002; Biswas et al. 2007; Zhang et al. 2008b) statistical analysis revealed significant negative correlation between estuarine dissolved CH$_4$ levels with respective salinity (Premonsoon: $R^2 = 89.1\%$, $F = 49.15$, $p < 0.001$, $n = 8$; Monsoon: $R^2 = 95.2\%$, $F = 120.12$, $p < 0.001$, $n = 8$; Postmonsoon: $R^2 = 75.8\%$, $F = 18.83$, $p = 0.005$, $n = 8$) indicating salinity is the major controlling factor for variability of CH$_4$ levels in this estuary. Moreover, the stronger degree of correlation during monsoon months compare to others indicates fresh water runoff mediated addition of CH$_4$ to the estuary during this period. Other than salinity, statistically no significant correlation was obtained with other physicochemical and biological variables ($[\text{CH}_4] = -297 - 0.14 \text{ temperature} + 58 \text{ pH} + 2.69 \text{ [chlorophyll]} - 19.1 \text{ [dissolved oxygen]} + 8.5 (\text{NPP/R}) \ [R^2 = 75\%$, $F = 1.20$, $p = 0.513$, $n = 24])$ (table 5); pointed towards in situ methanogenesis is not occurring within this estuary and estuarine dissolved CH$_4$ is entirely exogenous in nature (Dutta et al., 2015b).

Being well oxygenated, the water column presumably restrained methanogenesis but induced methanotrophy. CH$_4$ oxidation in the subsurface water was studied based on time dependent CH$_4$ reduction in the incubated samples and during this experiment none of the samples showed time series
increment of CH$_4$ concentration i.e. net CH$_4$ production. Specific rate of CH$_4$ oxidation (0.009 ± 0.001 to 0.018 ± 0.001 hr$^{-1}$) and consumption (0.54 ± 0.12 to 1.26 ± 0.27 nmol L$^{-1}$ hr$^{-1}$) in estuarine surface water was distinctly seasonal; having maximal premonsoon and minimal postmonsoon periods (Fig. 7F).

The mean dissolved CH$_4$ consumption rate was 20.59 nmol L$^{-1}$ d$^{-1}$, about 8.11 times lower than rate of CH$_4$ oxidation reported in the freshwater region of the Hudson estuary during summer (167 nmol L$^{-1}$ d$^{-1}$) (De Angelis and Scranton 1993). Aquatic CH$_4$ oxidation is a microbial process, so, the physicochemical parameters like temperature (thermal), salinity (tonicity), oxygen (oxidative), DIN (nutrient) and turbidity (surface) may have significant metabolic effects in this process. Moreover, other biological processes like primary production and community respiration may be considered to be influencing for this microbial process. Influence of salinity on dissolved CH$_4$ oxidation rate has been reported previously by de Angelis & Scranton 1993. According to their observation in Hudson estuary, high oxidation rates (4 to 167 nmol L$^{-1}$ d$^{-1}$) were found only at salinities below 6, rates at higher salinities being 1 to 2 orders of magnitude lower. The value for dissolved O$_2$ was significantly above the range of the estimated half-saturation constant for CH$_4$ oxidation, $K_m$ (0.5 - 0.8 mg L$^{-1}$; Lidstrom and Somers 1984) or the reported optimum range of 0.1-1.0 mg L$^{-1}$ (Rudd and Hamilton 1975) for microbial CH$_4$ oxidation in the water column. Influences of dissolved inorganic nitrogen (DIN) concentration on microbial CH$_4$ oxidation had been reported previously in Lake 227 (Rudd and Hamilton 1979). According to their observation in the presence of O$_2$ concentrations > 31 µM bacterial CH$_4$ oxidation was inhibited when DIN concentration was low (< 3 µM) as methanotrophs can fix nitrogen under low
DIN conditions (< 3µM). The nitrogen fixation is disrupted by high concentrations of O₂ but not inhibited when DIN concentration reaches to 20 µM. Moreover, turbid condition of the estuary methanotrophs associated with particulate matter can encounter high dissolved CH₄ levels in estuarine water column (Abil et al. 2007).

A multiple regression analysis was done in order to point out key controlling factor for CH₄ oxidation in this mangrove dominated estuary. Here the dependent variable is dissolved CH₄ oxidation rate ([CH₄]DOX) and independent variables are water temperature (T), salinity (S), dissolved oxygen (DO), dissolved inorganic nitrogen (DIN), net heterotrophy (R/P) and secchi disc depth (SD). The resultant regression equation between these variables ([CH₄]DOX = - 65.9 + 0.756 T - 2.18 S + 7.53 DO - 0.408 DIN - 2.01 P/R - 0.304 SD [R² = 91.6%, F = 9.12, p = 0.014, n = 12]) revealed significant correlation between [CH₄]DOX with S, DO & SD (table 6); indicating cumulative influence of these variables on variability of [CH₄]DOX in this estuarine water.

In a study of CH₄ oxidation in a freshwater lake, Panganiban et al. 1979 reported that 30-60% of the CH₄ oxidized was incorporated with the cell under aerobic conditions but essentially none was incorporated under anaerobic conditions. Rudd and Taylor, 1980 reported an incorporation percentage of 50% in a study of CH₄ oxidation in a freshwater lake. In the mangrove dominated estuary of Sundarbans, the CH₄ oxidation in the water column progressed at aerobic conditions. Assuming that 30-50% of the CH₄ carbon oxidized by methanotrophs was converted to organic matter (bacterial cell materials) and the remainder to CO₂. The mean CH₄ carbon converted to bacterial cell material was
computed as 0.59 mg C m\(^{-2}\) d\(^{-1}\) while primary productivity mediated production of organic carbon was 1545 mg C m\(^{-2}\) d\(^{-1}\). Thus, the production of organic carbon as a result of CH\(_4\) oxidation was only 0.038\% of that generated by primary production at that time. The remaining oxidised CH\(_4\) is quantitatively converted to less radiatively active CO\(_2\) & plays a crucial role in the estuarine carbon cycle. Using the stoichiometric equation for aerobic CH\(_4\) oxidation mechanism, CH\(_4\) oxidation mediated CO\(_2\) production rate in this mangrove dominated estuary was 3.25 mg m\(^{-2}\) d\(^{-1}\). Extrapolating the value for entire Sundarbans estuaries, total CO\(_2\) production from CH\(_4\) oxidation mechanism was 2.13 Gg yr\(^{-1}\).

Surface water CH\(_4\) % of saturation was ranged from 2483.02 ± 950.18 to 3525.45 ± 1053.72; indicating the estuarine water was CH\(_4\) supersaturated inducing CH\(_4\) exchange across water – atmosphere interface. Monthly variation of air – water CH\(_4\) flux and CH\(_4\) concentration in estuarine surface water are presented graphically in Fig.7E. Air – water CH\(_4\) fluxes from this estuary ranged between 6.27 ± 1.61 and 10.67 ± 6.92 µmol m\(^{-2}\) d\(^{-1}\); having minimal premonsoon and maximal monsoon periods (Dutta et al., 2015b). Minimal premonsoon CH\(_4\) fluxes may be attributed to the lowest value of wind speed over the estuary as well as surface water dissolved CH\(_4\) levels. Flux values estimate for this site fall within the range measured in the Hooghly estuary (0.88 – 148.63 µmol m\(^{-2}\) d\(^{-1}\)) (Biswas et al. 2007) but are much lower than those reported for some other estuaries like Oregon estuary (181.3 µmol m\(^{-2}\) d\(^{-1}\)) (De Angelis and Lilley, 1987). The large variation in water – atmosphere CH\(_4\) flux between different estuaries reflects a combination of dissolved CH\(_4\) concentration, the gas transfer velocity and variability of estuarine regimes (Dutta et al., 2015b). Wind speed over the estuarine water surface ranged between
The value seems to be low; may be due to high resistance offered by the mangrove vegetation resulting low gas transfer velocity as well as air-water CH$_4$ exchange flux value in this estuary. Our flux estimates were analyzed statistically to examine the influence of temperature and salinity on their variability. In both cases the analysis revealed significant correlations (water temperature: $R^2 = 61\%$, $F = 6.71$, $p = 0.029$, $n = 24$; salinity: $R^2 = 54\%$, $F = 5.31$, $p = 0.037$, $n = 24$) indicating a cumulative effect of temperature and salinity on estuarine CH$_4$ emission (Dutta et al., 2015b).

### 4.3. Atmospheric CH$_4$ dynamics:

Temperature of the mangrove forest atmosphere varied between 17.34 ± 4.0 to 30.34 ± 0.91°C at 10 m and 16.17 ± 1.80 to 29.73 ± 1.13°C at 20 m; being maximal premonsoon and minimal postmonsoon seasons (table 7). Wind velocity varied between 0.41 ± 0.36 and 1.32 ± 1.11 m s$^{-1}$ at 10 m height and 0.80 ± 0.88 to 1.64 ± 1.37 m s$^{-1}$ at 20 m height; having maximal monsoon and minimal postmonsoon periods. The atmospheric turbulence expressed by friction velocity ($U^*$) plays an important role in controlling the stability of the atmosphere & varied between 0.01 and 1.2 m s$^{-1}$. Planetary boundary layer or atmospheric boundary layer (PBL) height over the mangrove forest atmosphere varied between 702.45 m and 936.59 m; having maximal height during premonsoon and minimal during monsoon periods. Mean atmospheric boundary layer height over the tropical mangrove forest atmosphere was 811.7 m on annual basis. Values of other micrometeorological indices such as drag coefficient and
roughness height are presented in table 5. The seasonal variation for drag co-efficient may be attributed to the variation of wind speed in this mangrove forest atmosphere (Smith and Banke, 1975) while the values for both drag coefficient and roughness height were minimum in monsoon period. The low values of drag coefficient and roughness length could be deemed specific for this particular surface which is due to the action of low - pressure force on individual surface elements and the low shearing stress generated by particular wind (Mukhopadhyay et al., 2002).

Monthly variation of CH₄ mixing ratio at 10 & 20 m heights of the forest atmosphere are presented in Fig.8A; indicating minimal premonsoon (at both 10 and 20 m heights) and maximal during monsoon and postmonsoon periods for 10 m and 20 m heights, respectively (table 7). The maximal monsoon CH₄ mixing ratio at 10 m height may be attributed to maximum monsoon CH₄ emission from sediment and aquatic surfaces and primarily it’s mixing to the lower atmosphere of the mangrove ecosystem. Diurnal variation of CH₄ in the mangrove forest atmosphere at 10 m and 20 m heights in a month of January is presented in Fig.8B; indicating peak concentrations during early morning may be attributed to CH₄ accumulation within a stable boundary layer in that period (Dutta et al., 2013c). With progress of the day due to increment of atmospheric turbulence the stable layer breaks up resulting decrease of CH₄ concentration in the lower atmosphere (Mukhopadhyay et al. 2002). Changes in the micrometeorological parameters at the study site change the stability (Z/L) of the atmosphere, which in turn may alter the atmospheric CH₄ mixing ratio in the lower atmosphere ([CH₄]₁₀m). Statistical analysis revealed significant correlation between Z/L and [CH₄]₁₀m ([CH₄]₁₀m = 2.56 + 2.25 Z/L [R² = 74.8%, p
indicates potential impact of micrometeorological parameters on variability of CH$_4$ mixing ratio at lower atmosphere. Comparing CH$_4$ distribution along vertical column of the forest atmosphere it was evident that CH$_4$ mixing ratio at 10 m height was 1.02 times higher than 20 m height; induces biosphere – atmosphere CH$_4$ exchange in this mangrove environment depending upon micrometeorological conditions of the atmosphere. Monthly variation of biosphere – atmosphere CH$_4$ exchange flux is presented in Fig.8C having maximal flux monsoon and minimal postmonsoon periods. This mangrove biosphere acts as a source for CH$_4$ during monsoon, when $\Delta \chi$ is significantly positive and as sink during pre and post monsoon seasons, when $\Delta \chi$ is negative. The contributory processes to the $\Delta \chi$ are emission from water and soil resulting enrichment in the 10 m layer and oxidation (both microbial and photochemical) causing depletion at 10 and 20 m, respectively (Dutta et al. 2013). Mean biosphere – atmosphere methane exchange flux was calculated as 0.086 mg m$^{-2}$ d$^{-1}$; indicates on annual mean basis the mangrove ecosystem acts as a source of CH$_4$ to the upper atmosphere. Mean compensation point (i.e. where net biosphere - atmosphere CH$_4$ flux is zero) for CH$_4$ in this subtropical mangrove forest was 1.997 ppmv. Statistical analysis was done between biosphere – atmosphere CH$_4$ flux ($F_{BA}$) and sensible heat flux (H) as the transport of energy and mass are partially controlled by ‘H’. The regression equation [$F_{BA} = -0.0013 \ H^2 + 0.0967 \ H + 0.7789$ ($R^2 = 0.53$, F = 7.72, $p = 0.002$, n = 12)] explains 53% variability between dependent & independent variables indicating significant influence of sensible heat flux on variability of biosphere – atmosphere CH$_4$ exchange in this tropical mangrove forest ecosystem.
On annual basis mean daytime CH$_4$ mixing ratio was 1.03 times lower than night-time; the variability is presumed to be governed by photo-oxidation and diurnal changes in the boundary layer height. But statistically no significant correlation was obtained between variability of daytime and nighttime CH$_4$ mixing ratio with PBL height ($\Delta$CH$_4$ = - 0.0118$\Delta$PBL + 0.3045, $R^2$ = 16.2%, $F = 0.321$, $p = 0.987$, $n = 12$); indicating variability of atmospheric boundary layer height was not the major controlling factor for $\Delta$CH$_4$, that pointed towards large atmospheric CH$_4$ photo-oxidation in the mangrove forest atmosphere. CH$_4$ photo-oxidation rate in this subtropical mangrove forest atmosphere varied between $6.05 \times 10^{10}$ and $1.67 \times 10^{11}$ molecules cm$^{-3}$ d$^{-1}$ being maximum oxidation during monsoon and minimum during postmonsoon periods (Dutta et al. 2015c). The peak monsoon CH$_4$ photo-oxidation rate may be attributed to maximum CH$_4$ supply through emission as well as high UV index and UV erythermal dose irradiance during this period in these subtropical latitudes (Panicker et al. 2014). Considering the mean day light period as 12 hours and $6.023 \times 10^{23}$ molecules equals to 1 mole or 16000 mg CH$_4$, the mean CH$_4$ photo-oxidation rate in this tropical mangrove forest atmosphere was calculated as $3.25 \times 10^{-9}$ mg cm$^{-3}$ d$^{-1}$.

**4.4: Quantitative CH$_4$ budget from Indian Sundarbans:**

A box diagram (fig.9) was constructed for describing biogeochemical CH$_4$ cycling in Sundarbans biosphere reserve. In the model different subsystems are designated as separate reservoir. CH$_4$ storage in each reservoir and exchange fluxes of CH$_4$ between different reservoirs are presented as an annual mean
and values were used to calculate the input and output of CH$_4$ to/from the reservoirs, which in turn established the CH$_4$ budget for this mangrove-dominated estuarine system.

**Mangrove sediment methane budget:**

1. Mean CH$_4$ production potential in intertidal forest sediment (up to the depth of 25 cm) was 3547 µmol m$^{-3}$ d$^{-1}$. Considering the rate equal to in situ CH$_4$ production and extrapolating over entire forest, total CH$_4$ production within 25 cm depth of the forest sediment is 21.75 Ggyr$^{-1}$.

2. Intertidal sediment pore water CH$_4$ concentration was 3451 nM and extrapolating the concentration for entire mangrove forest (up to 25 cm depth), the sediment stands as a reservoir pool of 0.031Gg CH$_4$.

3. The intertidal sediment pore water methane concentration was about 55 times supersaturated than adjacent estuarine water (63.04 nM) indicating significant out-flux of CH$_4$ rich pore water from intertidal sediment to estuary during low tide phase via advective transport.

4. About 8.2% of the produced CH$_4$ is advectively transported to the adjacent estuarine system with a rate of 159.52 µmol m$^{-2}$ d$^{-1}$.

5. Mean CH$_4$ oxidation potential at intertidal forest sediment surface was 1.758 mg m$^{-2}$ d$^{-1}$ and total oxidation was 2.70 Ggyr$^{-1}$, when extrapolated for entire forest area of Sundarbans. The
value indicates only 12.41% of produced CH\textsubscript{4} is oxidized at sediment surface; presenting petite activity of methanotrophs in comparison to the methanogens in forest sediment.

6. Total CH\textsubscript{4} emission across sediment – atmosphere interface of the mangrove forest was 10.8 Ggyr\textsuperscript{-1} (about 49.6\% of total produced CH\textsubscript{4} in sediment) with a rate of 7.06 mg m\textsuperscript{-2} d\textsuperscript{-1}.

7. The total CH\textsubscript{4} emission and oxidation from/at the mangrove surface sediment was 6.05 and 1.51 times higher, respectively compare to total CH\textsubscript{4} advectively transported to the estuary; indicates emission acts as major CH\textsubscript{4} removal pathway from intertidal mangrove sediment.

8. Balancing total production and removal, annually 6.46 GgCH\textsubscript{4} remains unexplained. This establishes the existence of anaerobic methane oxidation in mangrove sediment column which was not covered in this study.

**Sub-tidal sediment CH\textsubscript{4} budget:**

1. CH\textsubscript{4} production potential of 0 – 5 cm depth of estuarine underlying sediment (sub-tidal sediment) was 48.88 µmol m\textsuperscript{-3} d\textsuperscript{-1} and total production was 0.026 Ggyr\textsuperscript{-1} when extrapolated for entire sub-tidal area for estuaries of Sundarbans.

2. Mean sub-tidal sediment (0 – 5 cm) pore water CH\textsubscript{4} concentration was 3286 nM; which was about 52.13 times supersaturated than overlying estuarine water inducing diffusive CH\textsubscript{4} transport from sub-tidal sediment to the overlying estuary.
3. Mean diffusive CH$_4$ flux from sub-tidal sediment to the overlying estuary was 8.45 µmol m$^{-2}$ d$^{-1}$. Extrapolating the rate for entire sub-tidal area of Sundarbans, the sub-tidal sediment acts as a source of 0.089 GgCH$_4$ annually to the upper estuarine system.

**Estuarine CH$_4$ budget:**

1. Total CH$_4$ input from sediment to estuary (by both advection and diffusion transports) was 1.875Gg yr$^{-1}$. Advective flux being 20 times higher than diffusive flux acts as major source for CH$_4$ to the estuary.

2. Mean dissolved CH$_4$ concentration in the estuary was 63.04 nM. Extrapolating this over the entire volume of the estuaries of the Sundarbans, the system stands as a reserve pool of 0.011Gg CH$_4$ (Dutta et al., 2015b).

3. The total CH$_4$ oxidation rate in the estuarine water column was 1.30Ggyr$^{-1}$ with a rate of 20.59 nmol L$^{-1}$ d$^{-1}$.

4. Mean CH$_4$ emission flux across the water - atmosphere interface of the estuary was 8.88 µmol m$^{-2}$ d$^{-1}$. Extrapolating this over the total estuarine surface area, on an annual basis the mangrove associated estuaries of the Sundarbans are a source of 0.093Gg CH$_4$ to the regional atmosphere, which is only 4.96 % of total CH$_4$ supplied to the estuary.
5. CH₄ oxidation, being 14 times higher than water-atmosphere exchange, is considered as the principal CH₄ removal mechanism in this estuary.

6. Mean turnover time of CH₄ in the water column relative to oxidation and emission was 3.77 days, which is in the range of turnover times relative to oxidation reported for the low salinity region of the Hudson estuary (1.4 – 9 days) (De Angelis and Scranton 1993).

7. The total sink of CH₄ due to these oxidation and emission processes were 1.39 Ggyr⁻¹, about 74.13% of total CH₄ supply to the estuary, indicating a significant export flux of CH₄ from estuary to the adjacent continental shelf.

8. Balancing CH₄ sources vs. sinks in this estuarine system, the export flux of CH₄ from estuary to the continental shelf was 0.485 Ggyr⁻¹, indicating a significant contribution from the Sundarbans estuaries to the CH₄ budget of the northern Bay of Bengal (Dutta et al., 2015b).

**Atmospheric CH₄ budget:**

1. Net CH₄ emission from Sundarbans mangrove ecosystem (sediment & estuarine surfaces) to the regional atmosphere was 10.89 Ggyr⁻¹, of which sediment is the principal contributor (99.17%).

2. Comparison to the global mean CH₄ emission rate from mangrove forest & creeks (10.76 mg m⁻² d⁻¹; Barnes et al., 2006) mean CH₄ emission rate from Sundarbans mangrove environment is
approximately 2.99 times lower; representing partial impact of this mangrove system towards earth’s global warming as well as climate change scenario.

3. Atmospheric CH\textsubscript{4} mixing ratio in 10 m and 20 m heights of the forest atmosphere were 2.038 and 1.987 ppmv, respectively having mean of 2.013 ppmv. Extrapolating over entire Sundarbans up to the height of atmospheric boundary layer (811.7 m), atmosphere stands as a reservoir pool of 11.2 GgCH\textsubscript{4}.

4. The annual mean mangrove biosphere atmosphere CH\textsubscript{4} exchange flux was 0.086 mg m\textsuperscript{-2} d\textsuperscript{-1} and the former when multiplied by the total forest area of the Sundarbans yields that this tropical mangrove ecosystem annually acts as source for 0.30 GgCH\textsubscript{4} to the regional atmosphere (about 2.75% of total CH\textsubscript{4} input from water & sediment surfaces).

5. Total CH\textsubscript{4} photo-oxidation in the forest atmosphere up to height of atmospheric boundary layer was 9.26 Ggyr\textsuperscript{-1} with a mean rate of 3.25 x 10\textsuperscript{-9} mg cm\textsuperscript{-3} d\textsuperscript{-1}. Compare to total CH\textsubscript{4} supply to the forest atmosphere, about 85% is photo-oxidized within atmospheric boundary layer of Sundarbans and is recognized as major atmospheric CH\textsubscript{4} removal pathway. The photo-oxidation mediated depletion of CH\textsubscript{4} is highly significant in atmospheric chemistry producing byproducts like HCHO, O\textsubscript{3} depending upon ambient NO\textsubscript{x} level. Balancing total atmospheric sources and sinks, annually 1.33Gg CH\textsubscript{4} remains unbalanced in the atmosphere, which enriches regional atmospheric CH\textsubscript{4} mixing ratio.

5. Conclusion:

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CH$_4$ production potential within 25 cm depth of the forest sediment is 21.75 Ggyr$^{-1}$ and pore water CH$_4$ concentration was 3541 nM. CH$_4$ fluxes across intertidal sediment – atmosphere interface acts as major sink for produced CH$_4$ in intertidal sediment over surface layer CH$_4$ oxidation and advective CH$_4$ transport to estuary. The process of methanogenesis is totally restricted within estuarine water column and is supplied from adjacent mangrove forest ecosystem and underlying sediment of the estuary. Advective flux being 20 times higher than diffusive flux acts as major source for CH$_4$ to the estuary. CH$_4$ oxidation, being 14 times higher than water - atmosphere exchange, is considered the principal CH$_4$ removal mechanism in this estuary. Total annual CH$_4$ emission from sediment and water surfaces of the Sundarbans mangrove biosphere was 10.89Gg, of which sediment is the principal contributor (99.17%). Compare to total CH$_4$ supply to the atmosphere, about 85% is photo-oxidized within atmospheric boundary layer of Sundarbans and 2.75% is transported to the upper atmosphere through biosphere – atmosphere CH$_4$ exchange flux.

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Table 1: Seasonal variation of CH$_4$ production potential and pore water CH$_4$ concentrations in intertidal and sub-tidal sediments. Here, T = soil surface temperature; S = pore water salinity; [CH$_4$]$_{(PI)}$ = CH$_4$ production potential in intertidal sediment; IS = intertidal sediment; SS = sub-tidal sediment.

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<th>Season</th>
<th>T (°C)</th>
<th>S</th>
<th>Depth (cm)</th>
<th>[CH$<em>4$]$</em>{(PI)}$ (µmol m$^{-3}$ d$^{-1}$)</th>
<th>[CH$<em>4$]$</em>{(IS)}$ (µM)</th>
<th>[CH$<em>4$]$</em>{(SS)}$ (µM)</th>
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</thead>
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<td>15 – 20</td>
<td>4373.44</td>
<td>4508</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 – 25</td>
<td>5850.478</td>
<td>6587</td>
<td></td>
</tr>
<tr>
<td>Postmonsoon</td>
<td>18.25 ± 0.22</td>
<td>25.98 ± 0.45</td>
<td>0 – 5</td>
<td>ND</td>
<td>2246</td>
<td>3980 ± 1227</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 – 10</td>
<td>1175.56</td>
<td>2319</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 – 15</td>
<td>4033.30</td>
<td>2413</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15 – 20</td>
<td>5903.10</td>
<td>4542</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 – 25</td>
<td>7352.94</td>
<td>6670</td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Results of multiple regression analysis between pore water CH$_4$ concentrations, Eh, NO$_2^-$, SO$_4^{2-}$, AVS and organic carbon (OC) concentration.

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coef</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>10.601</td>
<td>2.921</td>
<td>3.63</td>
<td>0.005</td>
</tr>
<tr>
<td>Eh</td>
<td>-0.018447</td>
<td>0.009074</td>
<td>-2.03</td>
<td>0.013</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>-0.12277</td>
<td>0.05477</td>
<td>-2.24</td>
<td>0.052</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.00764</td>
<td>0.01454</td>
<td>-0.53</td>
<td>0.612</td>
</tr>
<tr>
<td>AVS</td>
<td>-0.06933</td>
<td>0.04129</td>
<td>-1.68</td>
<td>0.127</td>
</tr>
<tr>
<td>%OC</td>
<td>-4.086</td>
<td>1.086</td>
<td>-3.76</td>
<td>0.004</td>
</tr>
</tbody>
</table>
Table 3: Results of multiple regression analysis between surface layer CH$_4$ oxidation potential ([CH$_4$]$_{(ox)}$) vs. NH$_4^+$ & NO$_3^-$ concentrations.

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coef</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>1.6338</td>
<td>0.3253</td>
<td>5.02</td>
<td>0.015</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-0.3065</td>
<td>0.1362</td>
<td>-2.25</td>
<td>0.110</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.2930</td>
<td>0.1285</td>
<td>2.28</td>
<td>0.107</td>
</tr>
</tbody>
</table>
Table 4: Seasonal variation of dissolved CH$_4$ concentrations, physicochemical and biological parameters of estuarine water.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Parameters</th>
<th>Position</th>
<th>Premonsoon</th>
<th>Monsoon</th>
<th>Postmonsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[CH$_4$] (nM)</td>
<td>Surface</td>
<td>54.20 ± 5.06</td>
<td>64.58 ± 10.56</td>
<td>90.91 ± 21.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>47.28 ± 12.85</td>
<td>53.27 ± 19.47</td>
<td>67.97 ± 33.12</td>
</tr>
<tr>
<td>Physical</td>
<td>Temperature (°C)</td>
<td>Surface</td>
<td>29.99 ± 0.97</td>
<td>27.82 ± 0.26</td>
<td>19.88 ± 0.18</td>
</tr>
<tr>
<td>property</td>
<td></td>
<td>Bottom</td>
<td>28.79 ± 0.07</td>
<td>26.92 ± 0.62</td>
<td>19.08 ± 0.78</td>
</tr>
<tr>
<td></td>
<td>SD (cm)</td>
<td>Surface</td>
<td>62.3 ± 13.1</td>
<td>29.7 ± 7.8</td>
<td>75.9 ± 7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>28.79 ± 0.07</td>
<td>26.92 ± 0.62</td>
<td>19.08 ± 0.78</td>
</tr>
<tr>
<td>Chemical</td>
<td>Salinity</td>
<td>Surface</td>
<td>27.09 ± 0.59</td>
<td>19.06 ± 4.33</td>
<td>22.33 ± 0.81</td>
</tr>
<tr>
<td>properties</td>
<td></td>
<td>Bottom</td>
<td>26.88 ± 0.15</td>
<td>18.87 ± 0.33</td>
<td>22.14 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>DO (mg L$^{-1}$)</td>
<td>Surface</td>
<td>6.53 ± 0.29</td>
<td>6.04 ± 0.73</td>
<td>7.27 ± 1.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>5.83 ± 0.37</td>
<td>5.41 ± 0.03</td>
<td>5.98 ± 0.79</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>Surface</td>
<td>8.17 ± 0.16</td>
<td>8.10 ± 0.03</td>
<td>8.15 ± 0.06</td>
</tr>
<tr>
<td>Biological</td>
<td>Chl (µg L$^{-1}$)</td>
<td>Surface</td>
<td>5.30 ± 0.19</td>
<td>3.11 ± 0.39</td>
<td>7.88 ± 1.90</td>
</tr>
<tr>
<td>properties</td>
<td>P (mg C m$^{-2}$ hr$^{-1}$)</td>
<td>Surface</td>
<td>56.9 ± 7.1</td>
<td>48.2 ± 8.0</td>
<td>88.0 ± 18.6</td>
</tr>
<tr>
<td></td>
<td>R (mg C m$^{-2}$ hr$^{-1}$)</td>
<td>Surface</td>
<td>125.0 ± 100</td>
<td>102.8 ± 116.7</td>
<td>110.1 ± 65.6</td>
</tr>
</tbody>
</table>
Table 5: Results of multiple regression analysis between [CH$_4$] and temperature (T) (°C), pH, chlorophyll (Chl) (µg L$^{-1}$), dissolved oxygen (DO) (mg L$^{-1}$), productivity and community respiration ratio (P / R).

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coef</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>-296.8</td>
<td>986.5</td>
<td>-0.30</td>
<td>0.792</td>
</tr>
<tr>
<td>T</td>
<td>-0.140</td>
<td>2.178</td>
<td>-0.06</td>
<td>0.955</td>
</tr>
<tr>
<td>pH</td>
<td>57.6</td>
<td>103.1</td>
<td>0.56</td>
<td>0.633</td>
</tr>
<tr>
<td>Chl</td>
<td>2.688</td>
<td>5.801</td>
<td>0.46</td>
<td>0.689</td>
</tr>
<tr>
<td>DO</td>
<td>-19.13</td>
<td>28.82</td>
<td>-0.66</td>
<td>0.575</td>
</tr>
<tr>
<td>P / R</td>
<td>8.50</td>
<td>61.86</td>
<td>0.14</td>
<td>0.903</td>
</tr>
</tbody>
</table>
Table 6: Results of multiple regression analysis between dissolved methane consumption rate ([\(\text{CH}_4\)]_{\text{DOX}}) vs. water temperature (T), salinity (S), dissolved oxygen (DO), DIN, net heterotrophy (P/R) and secchi disc depth (S_d).

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coef</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>-65.85</td>
<td>22.24</td>
<td>-2.96</td>
<td>0.031</td>
</tr>
<tr>
<td>T</td>
<td>0.7561</td>
<td>0.6142</td>
<td>1.23</td>
<td>0.273</td>
</tr>
<tr>
<td>S</td>
<td>2.1752</td>
<td>0.4949</td>
<td>4.40</td>
<td>0.007</td>
</tr>
<tr>
<td>DO</td>
<td>7.528</td>
<td>2.868</td>
<td>2.62</td>
<td>0.047</td>
</tr>
<tr>
<td>DIN</td>
<td>-0.4082</td>
<td>0.3686</td>
<td>-1.11</td>
<td>0.318</td>
</tr>
<tr>
<td>P/R</td>
<td>-2.012</td>
<td>2.938</td>
<td>-0.68</td>
<td>0.524</td>
</tr>
<tr>
<td>S_d</td>
<td>-0.30365</td>
<td>0.09738</td>
<td>-3.12</td>
<td>0.026</td>
</tr>
</tbody>
</table>
Table 7: Seasonal variation of micrometeorological parameters, methane mixing ratio, biosphere – atmosphere CH$_4$ exchange and CH$_4$ photo-oxidation in mangrove forest atmosphere.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Height(m)</th>
<th>Premonsoon</th>
<th>Monsoon</th>
<th>Postmonsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air temp. (°C)</td>
<td>10</td>
<td>30.34 ± 0.91</td>
<td>29.74 ± 2.50</td>
<td>17.34 ± 4.09</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>29.73 ± 1.13</td>
<td>28.37 ± 0.88</td>
<td>16.17 ± 1.80</td>
</tr>
<tr>
<td>Wind velocity(ms$^{-1}$)</td>
<td>10</td>
<td>0.70 ± 0.42</td>
<td>1.32 ± 1.11</td>
<td>0.41 ± 0.36</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.95 ± 0.44</td>
<td>1.64 ± 1.37</td>
<td>0.80 ± 0.88</td>
</tr>
<tr>
<td>U* (m/sec)</td>
<td></td>
<td>0.20 ± 0.04</td>
<td>0.15 ± 0.15</td>
<td>0.17 ± 0.49</td>
</tr>
<tr>
<td>Z$_0$ (m)</td>
<td></td>
<td>3.77 ± 3.01</td>
<td>1.63 ± 1.02</td>
<td>2.97 ± 2.98</td>
</tr>
<tr>
<td>C$_D$(10m)</td>
<td></td>
<td>0.386</td>
<td>0.157</td>
<td>0.167</td>
</tr>
<tr>
<td>H (W m$^{-2}$)</td>
<td></td>
<td>6.349</td>
<td>8.248</td>
<td>1.154</td>
</tr>
<tr>
<td>PBL (m)</td>
<td></td>
<td>936.59</td>
<td>702.45</td>
<td>796.10</td>
</tr>
<tr>
<td>CH$_4$ (ppmv)</td>
<td>10</td>
<td>1.769 ± 0.04</td>
<td>2.180 ± 0.12</td>
<td>2.112 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.821 ± 0.09</td>
<td>2.027 ± 0.03</td>
<td>2.116 ± 0.06</td>
</tr>
<tr>
<td>F$_{BA}$ (mg m$^{-2}$ hr$^{-1}$)</td>
<td></td>
<td>- 4.514</td>
<td>6.635</td>
<td>-2.110</td>
</tr>
<tr>
<td>[CH$_4$] photo-ox rate (molecules cm$^{-3}$ d$^{-1}$)</td>
<td>10</td>
<td>1.40 x 10$^{11}$</td>
<td>1.67 x 10$^{11}$</td>
<td>6.05 x 10$^{10}$</td>
</tr>
</tbody>
</table>
Fig. 1: Schematic diagram of atmospheric CH$_4$ photooxidation with/without NO$_x$ concentration.
Fig. 2: Map showing locations of the study point.
The diagram illustrates the changes in Eh (mV) and SO$_4^{2-}$ concentration (mM) with depth.

- **Eh (mV)**:
  - Depth in cm: 0, 5, 10, 15, 20, 25
  - Eh values range from -300 to 0 mV

- **SO$_4^{2-}$ - S conc. (mM)**:
  - Depth in cm: 0, 5, 10, 15, 20, 25
  - SO$_4^{2-}$ concentration ranges from 0 to 90 mM

The graphs are labeled (A) and (B) for reference.
Fig. 3: Vertical variation of physicochemical properties of mangrove sediment (A) $E_h$ (B) pore water sulphate – S concentration (C) % organic carbon (D) pore water AVS concentration
Fig. 4: Seasonal variation of advective and diffusive CH$_4$ fluxes from intertidal and subtidal sediments, respectively.

Fig. 5: Seasonal variations of surface sediment CH$_4$ oxidation potential in mangrove sediment.
Fig. 6: Monthly variation of soil methane emission from intertidal mangrove forest.
Fig. 7: Monthly variation of physicochemical parameters along with dissolved methane concentrations, methane oxidation and air-water methane exchange flux.
8(B) 

CH$_4$ mixing ratio (ppmv)

- 10 m
- 20 m

6a.m 9 a.m 12 3 p.m 6 p.m 9 p.m 0 a.m 3 a.m

noon

8(C) 

Biome - atmosphere CH$_4$ flux (mg m$^{-2}$ d$^{-1}$)

Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

-15 -10 -5 0 5 10 15 20
Fig. 8: (A) Monthly variation of methane mixing ratio in forest atmosphere (B) Diurnal variation of methane mixing ratio in forest atmosphere (C) Monthly variation of biosphere-atmosphere methane exchange flux.

Fig. 9: Quantitative methane budget at Sundarbans mangrove ecosystem.