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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 CH_4 was studied in Sundarbans mangrove system during June 2010 to December 2012. The sediment was CH_4 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 CH_4 out-flux from sediment to estuary via advective and diffusive transports. Mean advective (from intertidal sediment) and diffusive (from sub-tidal sediment) CH_4 fluxes were 159.52 µmol m^{-2} d^{-1} and 8.45 µmol m^{-2} d^{-1}, respectively. Intertidal sediment CH_4 emission rate was about 4 times higher than surface layer CH_4 oxidation rate; indicating petite methanotrophic activity in mangrove sediment. Mean CH_4 concentration in estuarine surface and bottom waters were

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69.90 and 56.17nM, 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 2.013ppmv. 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

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35 in CH_4 emission from wetlands that contributes approximately 20 - 39% of the annual global CH_4
36 budget (Hoehler et al. 2014).

37 Presenting accurate wetland CH_4 budget is very important for projecting the future climate. But, the
38 primary problems in attempting to develop accurate CH_4 budget is the large spatial and temporal (Ding
39 et al. 2003) variability in CH_4 emissions that reported all over the world. Being an integrated part of
40 coastal wetlands, mangroves are relatively very less studied ecosystem with respect to CH_4
41 biogeochemistry (Barnes et al. 2006; Biswas et al. 2007; Bouillon et al. 2007c; Kristensen et al. 2008).
42 Consequently, presenting wider CH_4 and carbon budgets for mangrove ecosystem globally is
43 problematic.
44 Mangroves are one of the most productive coastal ecosystems and are characterized by high turnover
45 rates of organic matter, both in the water column and in sediment. The organic matter mineralization in
46 sediment is a multi-step process, which begins with an enzymatic hydrolysis of polymeric material to
47 soluble monomeric and oligomeric compounds. Under oxic conditions the organic carbon (OC) is
48 directly mineralized to carbon dioxide and water. But, the mangrove sediments are rich in clay content
49 that reduces the porosity of the sediment and helps in the formation and retention of anoxic condition
50 (Dutta et al. 2013). OC mineralization in anaerobic environment is typically complex involving various
51 microbes in initial de-polymerization followed by fermentative microbial break down of complex
52 organic compounds to small moieties. The end products of the fermentation process used by
53 methanogens in the final step of anaerobic decomposition can also be used by microbial groups that

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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 $\leq$ 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.

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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

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91 extensive natural mangrove forest was inscribed as a UNESCO world heritage site and covers an area of
92 10,200 sq. km of which 4200 sq. km of reserved forest is spread over India and rest part is in
93 Bangladesh. The Indian Sundarbans Biosphere Reserve (SBR) is extended over an area of 9600 km^2
94 constituted of 1800 sq km estuarine waterways and 3600 sq. km reclaimed areas along with above
95 stated mangrove reserve forest. The forest is about 140 km in length from east to west and extends
96 approximately 50 – 70 km from the southern margin of the Bay of Bengal towards the north. The Indian
97 part of the Sundarbans mangrove delta is crisscrossed by the estuarine phases of several rivers namely
98 Mooriganga, Saptamukhi, Thakuran, Matla, Bidya, Gosaba and Haribhanga forming a sprawling
99 archipelago of 102 islands out of which 54 are reclaimed for human settlement and rest are virgin. One
100 of these virgin Islands is the Lothian Island, which is situated at the buffer zone of the Sundarbans
101 Biosphere Reserve covering an area of 38 km^2. This island completely intertidal and occupied by thick,
102 robust and resilient mangroves trees with a mean height of < 10 m. Among the mangroves, *Avicennia*
103 *alba*, *Avicennia marina* and *Avicennia officinalis* are the dominant species, *Excoecaria agallocha* and
104 *Heritiera fomes* are thinly distributed and *Ceriops decandra* is found scattered all over the island. The
105 mangrove sediment is silty clay in nature and composed of quartzo-feldspathic minerals like quartz,
106 albite and microline. The adjacent estuarine system of the island is Saptamukhi which has no perennial
107 source of freshwater and receives significant amounts of agricultural and anthropogenic runoff
108 especially during monsoon. Climate in the study area is characterized by premonsoon (February –
109 May), south west monsoon (June – September) and north east monsoon or postmonsoon (October –

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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^o 42.58'N: 88^o18'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

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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.

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147 During low tide condition CH_4 emission from the intertidal sediment surface to the atmosphere was
148 measured using static Perspex chamber method (Purvaja et al. 2004). The chambers were placed in the
149 sediment for a particular duration and CH_4 emission rate was calculated based on the enrichment of CH_4
150 mixing ratio inside the chamber in comparison to the ambient air. Mixing ratio of CH_4 was measured by
151 gas chromatography as described earlier. Advective CH_4 fluxes from intertidal forest sediment to the
152 estuarine water column (F_{ISW}) were computed as (Reay et al. 1995): $F_{ISW} = \Phi \times \nu \times C$; where, Φ =
153 porosity of sediment = 0.58 (Dutta et al. 2013), ν = mean linear velocity = $d\Phi^{-1}$ (d = specific discharge),
154 C = pore water CH_4 concentration in intertidal sediment. The specific discharge for the intertidal
155 sediment was recorded by measuring the rate of accumulation of pore water in an excavated pit of
156 known surface area (Dutta et al. 2015b). This was done during low tide condition in the intertidal flat at
157 100 m intervals along with receding water level. Diffusive CH_4 flux from sub-tidal sediment to estuary
158 was calculated using Fick's law of diffusion (Sansone et al. 2004).

159 Collection and analysis of dissolved CH_4 concentration using gas chromatograph for estuarine water has
160 been described elsewhere (Dutta et al. 2013). For measurement of CH_4 oxidation water was filled in pre-
161 cleaned (acid washed and sterilized) septum fitted incubation bottles (in a batch of 12 bottles) from
162 Niskin samplers with gentle overflowing and sealed with no air bubbles. Immediately after collection
163 two bottles are poisoned with $HgCl_2$ to stop microbial CH_4 oxidation and they are considered as control
164 for the experiment. Rest of the bottles are kept for incubation in ambient condition with two bottles
165 withdrawn from incubation daily and were poisoned with saturated $HgCl_2$ solution to continue the

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incubation experiment up to a times series of 5 days. The concentrations of dissolved CH_4 in all incubated samples was measured to record a time series kinetics of CH_4 oxidation. From the time series plot, the specific rate of CH_4 oxidation was calculated by linear regression of the natural log of CH_4 concentration against time. The value of specific rate of CH_4 oxidation is equivalent to the slope of the regression line. Actual rates of CH_4 oxidation (CH_4 consumption rate) were calculated by the product of dissolved CH_4 concentration and specific rate of CH_4 oxidation (Utsumi et al. 1998b).

CH_4 flux across the air - water interface was calculated according to the expression (Liss and Merlivat 1986): $F_{WA}= k\ \Delta C$; where, ΔC is the difference in concentrations ($[CH_4]_{observed} - [CH_4]_{equilibrium}$) 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

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185 inorganic nitrogen concentration (DIN). For estimating of chlorophyll concentrations samples were
186 collected in 1L amber colored bottles and stored on ice during transportation to the laboratory. In the
187 laboratory chlorophyll concentration was measured using a standard spectrophotometric method
188 (Parsons et al. 1992). Primary productivity and community respiration in the estuarine surface water
189 were measured in situ by a light and dark bottle oxygen method (Parsons et al. 1992) with a relative
190 uncertainty of ± 2.5%.

191 Samples for measurement of CH_4 mixing ratio were collected in air sampling bulbs from both 10 m and
192 20 m heights and transported to laboratory for analysis. Samples were analyzed using gas
193 chromatography (Varian CP 3800GC) fitted with chrompack capillary column (12.5 m x 0.53 mm) and
194 a flame ionization detector (FID). Two reference gas standards (10.9 ppmv and 5 ppmv, supplied by
195 Chemtron Science Laboratories Pvt. Ltd) were used before and after every measurement. Duplicate
196 samples were analyzed periodically and the replicate measurements were found to be within 2 - 3.2 %.
197 Meteorological parameters like air temperature and wind velocity were simultaneously recorded at 10
198 and 20 m heights using a portable weather monitor (Model: Davis 7440) and the value was used to
199 calculated micrometeorological indices like friction velocity (U*), roughness height (Z_o), drag
200 coefficient and planetary boundary layer height (Ganguly et al. 2008). Biosphere - atmosphere CH_4
201 exchange flux (F_{BA}) was calculated using the following relation (Barrett 1998; Ganguly et al. 2008):

202 $$F_{BA} = V_C \, \Delta\chi.$$

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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 ($CH_4 + OH \rightarrow CH_3 + H_2O$) as: $P = k\,[CH_4]\,[OH]$; 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

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production potentials measured for this tropical mangrove forest sediment were within the range of that reported for pristine mangrove forest at Balandra, Maxico (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 CH_4 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 CH_4 production. In contrast, high premonsoon salinity regime of the ecosystem may partially inhibited CH_4 production potential of the system by supplying higher SO_4^{2-} and subsequent enhanced SO_4^{2-} 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 SO_4^{2-} 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).

CH_4 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

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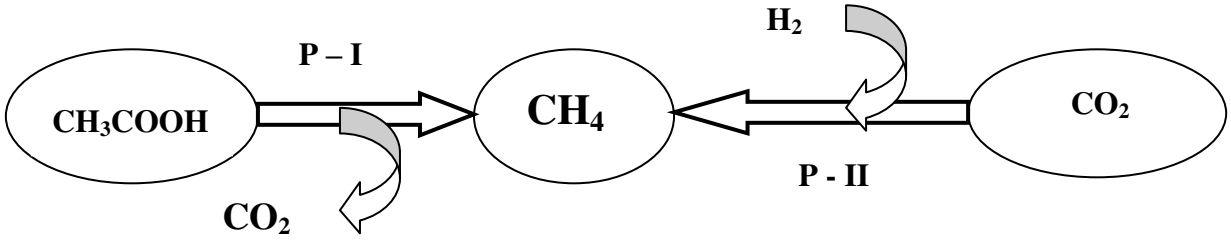
concentration during postmonsoon and minimum during premonsoon period. About 35.25 % higher OC supply in sub-tidal surface layer during postmonsoon period compare to premonsoon might have caused strong redox condition favoring a higher rate of CH_4 production.

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 CO_2 with H_2 (hydrogenotrophic). The pathways for both types of methanogenesis are as follows:



P – I = Acetoclastic methanogenesis; P – II = Hydrogenotrophic methanogenesis

Among these two, in high CO_2 rich environment acetoclastic methanogenesis is predominant over hydrogenotrophic one and approximately 70% of biologically produced CH_4 originates from conversion of the methyl group of acetate to CH_4 (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 CH_4. The estuarine bottom sediment was also OC as well as CO_2 rich and 0.82 mg m^{-3} d^{-1} of OC transformed through acetoclastic methanogenesis producing 34.22 µmol m^{-3} d^{-1} of CH_4. Extrapolating the values for entire Sundarbans, it

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257 is estimated that in the Sundarbans mangrove sediment (both inter and sub tidal sediments) about 22.86
258 $Ggyr^{-1}$ of OC was transformed through methanogenic pathway resulting 15.25 $Ggyr^{-1}$ of CH_4. The
259 mechanism also produces another radiatively active trace gas (CO_2) as a by-product of CH_4 production
260 & acetoclastic methanogenesis mediated CO_2 production rate of this mangrove forest sediment was
261 109.23 mg m^{-3} d^{-1}.

262 A major part of sedimentary produced CH_4 dissolves in the pore water at in situ high pressure resulting
263 significant super saturation (Dutta et al. 2013). Pore water CH_4 concentrations along intertidal forest
264 sediment depth profile are presented in table 1 indicating almost constant concentration up to 10 - 15 cm
265 sediment layer which abruptly increase 1.79 times at 15 - 20 cm depth and further increase to 2.26 –
266 2.76 times at 20 - 25 cm depth. On annual basis intertidal sediment pore water CH_4 concentrations
267 ranged between 3204 ± 1325 to 3639 ± 1949 nM, being maximal postmonsoon and minimal
268 premonsoon periods (Dutta et al., 2015b).

269 Statistical analysis (using MINITAB version 17) was performed between pore water CH_4 concentration
270 ($[CH_4]_{PW}$) vs. E_h, NO_2^-, SO_4^{2-}, AVS and organic carbon percentage (%OC) in order to point out key
271 controlling factor for variability of pore water CH_4 concentration in intertidal sediment. Here the
272 dependent variable is $[CH_4]_{PW}$ and independent variables are E_h, NO_2^-, SO_4^{2-}, AVS and % OC. The
273 regression equation between dependent and independent variables are as follows: $[CH_4]_{PW}$ = 10.6 -
274 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 =

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30). From the statistical analysis (table 2) it was found that $[CH_4]_{PW}$ was significantly correlated with %OC ($p = 0.004$) and E_h ($p = 0.013$) of sediment, indicating cumulative influence of %OC and E_h on variability of $[CH_4]_{PW}$ in this tropical mangrove forest.

Following same seasonal trend annual mean pore water 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 CH_4 supersaturated; induces significant CH_4 influx from intertidal & sub-tidal sediment to estuary. Advective 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 CH_4 flux may be ascribed to higher pore water CH_4 concentration as well as specific discharge (0.008 cm min^{-1}). Diffusive 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 CH_4 fluxes may be ascribed to maximal pore water CH_4 concentrations while the reverse case applies premonsoon.

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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 – 3.31μM 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).

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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^{o}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:

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

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

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

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331 bioturbation density in the forest area was counted as 45 ± 7 and 12 ± 2 nos. m^{-2}, respectively and
332 statistical analysis was done in order to examine the influence of pneumatophore and bioturbation on
333 emission of CH_4 in this mangrove forest atmosphere. Regression equations between soil CH_4 emission
334 rate (F_{SA}) vs. pneumatophores (P_{no}) and bioturbation (B_{no}) density were as follows:

335 $$\mathbf{F_{SA} = - 8.59 + 0.330\ P_{no}\ (R^2 = 81.9\%, F = 6.94, p = 0.032, n = 20)}$$

336 $$\mathbf{F_{SA} = 6.42 - 0.052\ B_{no}\ (R^2 = 61.9\%, F = 5.94, p = 0.041, n = 20)}$$

337 The statistical analysis revealed significant correlation between dependent & independent variables for
338 both cases indicating other than physicochemical factors, biological variables (like presence of
339 pneumatophore and bioturbation) also play a crucial role for CH_4 emission from the forest sediment.
340 The positive correlation between sediment CH_4 emission rate and pneumatophore density indicates
341 plant mediated emission of CH_4 in Sundarbans mangrove ecosystem whereas negative correlation with
342 bioturbation density indicates that burrows favored sediment oxygenation especially in surface layer,
343 resulting CH_4 oxidation in surface mangrove sediment and ultimately reduced its emission flux from
344 sediment. A similar observation on oxidation of surface sediment by crab burrows in the mangrove
345 environment was previously reported by Kristensen and Alongi, 2006.

346 **4.2 Estuarine CH_4 cycling:**

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347 Physicochemical and biological parameters of the estuarine water column are presented in table – 4 and
348 on monthly basis from Fig.7A to 7D. For both (temperature and salinity) the values were highest during
349 the premonsoon and lowest during the postmonsoon (for temperature) and monsoon (for salinity)
350 months. Marginal variation of temperature and salinity in estuarine surface and bottom water clearly
351 indicates a vertically well mixed water column. Surface water pH varied over a narrow range (8.10 ±
352 0.03 to 8.17 ± 0.16) and seasonal differences were not significant. Dissolved oxygen (DO)
353 concentrations in estuarine surface and bottom waters were high (6.04 ± 0.73 to 7.27 ± 1.14 mg L^{-1} and
354 5.41 ± 0.03 to 5.98 ± 0.79 mg L^{-1}, respectively) being maximal during postmonsoon and minimal during
355 monsoon periods. DO % of saturation varied between 94.8 and 99.3; indicates a well oxygenated water
356 column that would inhibit the anaerobic microbial metabolism of organic matter within estuarine water
357 column. The chlorophyll concentration in estuarine surface water ranged from 3.11 ± 0.39 to 7.88 ±
358 1.90 µg L^{-1} having highest and lowest concentrations during postmonsoon and monsoon, respectively.
359 Seasonal trends of chlorophyll concentration mirrored the changes in Secchi disc depth, which ranged
360 between 29.7 ± 7.8 and 75.9 ± 7.7 cm during the study period. The ratio between primary productivity
361 and community respiration was <1, indicates the estuary is net heterotrophic in nature.

362 During the observation period estuarine surface and bottom waters dissolved CH_4 concentrations ranged
363 from 54.20 ± 5.06 to 90.91 ± 21.20 and 47.28 ± 12.85 to 67.97 ± 33.12 nM, respectively (Fig.7E);
364 having maximal postmonsoon and minimal monsoon periods (table 4) (Dutta et al., 2015b). The CH_4
365 concentrations measured in this mangrove dominated estuary was within the range of that measured in

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366 Thames estuary, Loire estuary but higher than Hooghly estuary, Yangtze River estuary, Sado estuary
367 and Elbe estuary (Middelburg et al. 2002; Biswas et al. 2007; Zhang et al. 2008b). The peak
368 postmonsoon CH_4 concentrations may be attributed to cumulative effect of maximal supply of dissolved
369 CH_4 rich pore water from intertidal mangrove sediment and minimal CH_4 oxidation (will be discussed
370 later) in the estuarine water column. Like other tropical, sub-tropical and temperate estuaries (Upstill-
371 Goddard et al. 2000; Middelburg et al. 2002; Biswas et al. 2007; Zhang et al. 2008b) statistical analysis
372 revealed significant negative correlation between estuarine dissolved CH_4 levels with respective salinity
373 (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
374 = 8; Postmonsoon: $R^2 = 75.8\%$, $F = 18.83$, $p = 0.005$, n = 8) indicating salinity is the major controlling
375 factor for variability of CH_4 levels in this estuary. Moreover, the stronger degree of correlation during
376 monsoon months compare to others indicates fresh water runoff mediated addition of CH_4 to the estuary
377 during this period. Other than salinity, statistically no significant correlation was obtained with other
378 physicochemical and biological variables ($[CH_4]$ = - 297 - 0.14 temperature + 58 pH + 2.69
379 [chlorophyll] - 19.1 [dissolved oxygen] + 8.5 (NPP/R) [$R^2 = 75\%$, $F = 1.20$, $p = 0.513$, n = 24]) (table
380 5); pointed towards in situ methanogenesis is not occurring within this estuary and estuarine dissolved
381 CH_4 is entirely exogenous in nature (Dutta et al., 2015b).

382 Being well oxygenated, the water column presumably restrained methanogenesis but induced
383 methanotrophy. CH_4 oxidation in the subsurface water was studied based on time dependent CH_4
384 reduction in the incubated samples and during this experiment none of the samples showed time series

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385 increment of CH_4 concentration i.e. net CH_4 production. Specific rate of CH_4 oxidation (0.009 ± 0.001
386 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
387 water was distinctly seasonal; having maximal premonsoon and minimal postmonsoon periods (Fig.7F).
388 The mean dissolved CH_4 consumption rate was 20.59 nmol L^{-1} d^{-1} , about 8.11 times lower than rate of
389 CH_4 oxidation reported in the freshwater region of the Hudson estuary during summer (167 nmol L^{-1} d^{-1})
390 (De Angelis and Scranton 1993). Aquatic CH_4 oxidation is a microbial process, so, the
391 physicochemical parameters like temperature (thermal), salinity (tonicity), oxygen (oxidative), DIN
392 (nutrient) and turbidity (surface) may have significant metabolic effects in this process. Moreover, other
393 biological processes like primary production and community respiration may be considered to be
394 influencing for this microbial process. Influence of salinity on dissolved CH_4 oxidation rate has been
395 reported previously by de Angelis & Scranton 1993. According to their observation in Hudson estuary,
396 high oxidation rates (4 to 167 nmol L^{-1} d^{-1}) were found only at salinities below 6, rates at higher
397 salinities being 1 to 2 orders of magnitude lower. The value for dissolved O_2 was significantly above the
398 range of the estimated half-saturation constant for CH_4 oxidation, K_m (0.5 - 0.8 mg L^{-1}; Lidstrom and
399 Somers 1984) or the reported optimum range of 0.1-1.0 mg L^{-1} (Rudd and Hamilton 1975) for microbial
400 CH_4 oxidation in the water column. Influences of dissolved inorganic nitrogen (DIN) concentration on
401 microbial CH_4 oxidation had been reported previously in Lake 227 (Rudd and Hamilton 1979).
402 According to their observation in the presence of O_2 concentrations > 31 µM bacterial CH_4 oxidation
403 was inhibited when DIN concentration was low (< 3 µM) as methanotrophs can fix nitrogen under low

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404 DIN conditions (< 3µM). The nitrogen fixation is disrupted by high concentrations of O_2 but not
405 inhibited when DIN concentration reaches to 20 µM. Moreover, turbid condition of the estuary
406 methanotrophs associated with particulate matter can encounter high dissolved CH_4 levels in estuarine
407 water column (Abil et al. 2007).

408 A multiple regression analysis was done in order to point out key controlling factor for CH_4 oxidation in
409 this mangrove dominated estuary. Here the dependent variable is dissolved CH_4 oxidation rate
410 ($[CH_4]_{DOX}$) and independent variables are water temperature (T), salinity (S), dissolved oxygen (DO),
411 dissolved inorganic nitrogen (DIN), net heterotrophy (R/P) and secchi disc depth (S_d). The resultant
412 regression equation between these variables ($[CH_4]_{DOX}$ = - 65.9 + 0.756 T - 2.18 S + 7.53 DO - 0.408
413 DIN - 2.01 P/R - 0.304 S_d [R^2 = 91.6%, F = 9.12, p = 0.014, n = 12]) revealed significant correlation
414 between $[CH_4]_{DOX}$ with S, DO & S_d (table 6); indicating cumulative influence of these variables on
415 variability of $[CH_4]_{DOX}$ in this estuarine water.

416 In a study of CH_4 oxidation in a freshwater lake, Panganiban et al. 1979 reported that 30-60% of the
417 CH_4 oxidized was incorporated with the cell under aerobic conditions but essentially none was
418 incorporated under anaerobic conditions. Rudd and Taylor, 1980 reported an incorporation percentage
419 of 50% in a study of CH_4 oxidation in a freshwater lake. In the mangrove dominated estuary of
420 Sundarbans, the CH_4 oxidation in the water column progressed at aerobic conditions. Assuming that 30-
421 50% of the CH_4 carbon oxidized by methanotrophs was converted to organic matter (bacterial cell
422 materials) and the remainder to CO_2. The mean CH_4 carbon converted to bacterial cell material was

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423 computed as 0.59 mg C m^{-2} d^{-1} while primary productivity mediated production of organic carbon was
424 1545 mg C m^{-2} d^{-1}. Thus, the production of organic carbon as a result of CH_4 oxidation was only
425 0.038% of that generated by primary production at that time. The remaining oxidised CH_4 is
426 quantitatively converted to less radiatively active CO_2 & plays a crucial role in the estuarine carbon
427 cycle. Using the stoitiometric equation for aerobic CH_4 oxidation mechanism, CH_4 oxidation mediated
428 CO_2 production rate in this mangrove dominated estuary was 3.25 mg m^{-2} d^{-1}. Extrapolating the value
429 for entire Sundarbans estuaries, total CO_2 production from CH_4 oxidation mechanism was 2.13Gg yr^{-1}.

430 Surface water CH_4 % of saturation was ranged from 2483.02 ± 950.18 to 3525.45 ± 1053.72; indicating
431 the estuarine water was CH_4 supersaturated inducing CH_4 exchange across water – atmosphere
432 interface. Monthly variation of air – water CH_4 flux and CH_4 concentration in estuarine surface water
433 are presented graphically in Fig.7E. Air – water CH_4 fluxes from this estuary ranged between 6.27 ±
434 1.61 and 10.67 ± 6.92 µmol m^{-2} d^{-1}; having minimal premonsoon and maximal monsoon periods (Dutta
435 et al., 2015b). Minimal premonsoon CH_4 fluxes may be attributed to the lowest value of wind speed
436 over the estuary as well as surface water dissolved CH_4 levels. Flux values estimate for this site fall
437 within the range measured in the Hooghly estuary (0.88 – 148.63 µmol m^{-2} d^{-1}) (Biswas et al. 2007) but
438 are much lower than those reported for some other estuaries like Oregon estuary (181.3 µmol m^{-2} d^{-1})
439 (De Angelis and Lilley, 1987). The large variation in water – atmosphere CH_4 flux between different
440 estuaries reflects a combination of dissolved CH_4 concentration, the gas transfer velocity and variability
441 of estuarine regimes (Dutta et al., 2015b). Wind speed over the estuarine water surface ranged between

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442 2.28 ± 1.01 and 3.16 ± 1.79 ms^{-1}. The value seems to be low; may be due to high resistance offered by
443 the mangrove vegetation resulting low gas transfer velocity as well as air - water CH_4 exchange flux
444 value in this estuary. Our flux estimates were analyzed statistically to examine the influence of
445 temperature and salinity on their variability. In both cases the analysis revealed significant correlations
446 (water temperature: R^2 = 61%, F = 6.71, p = 0.029, n = 24; salinity: R^2 = 54%, F = 5.31, p = 0.037, n =
447 24) indicating a cumulative effect of temperature and salinity on estuarine CH_4 emission (Dutta et al.,
448 2015b).

449 **4.3. Atmospheric CH_4 dynamics:**

450 Temperature of the mangrove forest atmosphere varied between 17.34 ± 4.0 to 30.34 ± 0.91^oC at 10 m
451 and 16.17 ± 1.80 to 29.73 ± 1.13^oC at 20 m; being maximal premonsoon and minimal postmonsoon
452 seasons (table 7). Wind velocity varied between 0.41 ± 0.36 and 1.32 ± 1.11 m s^{-1} at 10 m height and
453 0.80 ± 0.88 to 1.64 ± 1.37 m s^{-1} at 20 m height; having maximal monsoon and minimal postmonsoon
454 periods. The atmospheric turbulence expressed by friction velocity (U*) plays an important role in
455 controlling the stability of the atmosphere & varied between 0.01 and 1.2 m s^{-1}. Planetary boundary
456 layer or atmospheric boundary layer (PBL) height over the mangrove forest atmosphere varied between
457 702.45 m and 936.59 m; having maximal height during premonsoon and minimal during monsoon
458 periods. Mean atmospheric boundary layer height over the tropical mangrove forest atmosphere was
459 811.7 m on annual basis. Values of other micrometeorological indices such as drag coefficient and

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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 CH_4 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 CH_4 mixing ratio at 10 m height may be attributed to maximum monsoon CH_4 emission from sediment and aquatic surfaces and primarily it's mixing to the lower atmosphere of the mangrove ecosystem. Diurnal variation of CH_4 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 CH_4 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 CH_4 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 CH_4 mixing ratio in the lower atmosphere ($[CH_4]_{10m}$). Statistical analysis revealed significant correlation between Z/L and $[CH_4]_{10m}$ ($[CH_4]_{10m}$ = 2.56 + 2.25 Z/L [R^2 = 74.8%, p

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479 < 0.001, F = 29.73, n = 30]); indicates potential impact of micrometeorological parameters on
480 variability of CH_4 mixing ratio at lower atmosphere. Comparing CH_4 distribution along vertical column
481 of the forest atmosphere it was evident that CH_4 mixing ratio at 10 m height was 1.02 times higher than
482 20 m height; induces biosphere – atmosphere CH_4 exchange in this mangrove environment depending
483 upon micrometeorological conditions of the atmosphere. Monthly variation of biosphere – atmosphere
484 CH_4 exchange flux is presented in Fig.8C having maximal flux monsoon and minimal postmonsoon
485 periods. This mangrove biosphere acts as a source for CH_4 during monsoon, when $\Delta\chi$ is significantly
486 positive and as sink during pre and post monsoon seasons, when $\Delta\chi$ is negative. The contributory
487 processes to the $\Delta\chi$ are emission from water and soil resulting enrichment in the 10 m layer and
488 oxidation (both microbial and photochemical) causing depletion at 10 and 20 m, respectively (Dutta et
489 al. 2013). Mean biosphere – atmosphere methane exchange flux was calculated as 0.086 mg m^{-2} d^{-1};
490 indicates on annual mean basis the mangrove ecosystem acts as a source of CH_4 to the upper
491 atmosphere. Mean compensation point (i.e. where net biosphere - atmosphere CH_4 flux is zero) for CH_4
492 in this subtropical mangrove forest was 1.997 ppmv. Statistical analysis was done between biosphere –
493 atmosphere CH_4 flux (F_{BA}) and sensible heat flux (H) as the transport of energy and mass are partially
494 controlled by 'H'. The regression equation [F_{BA} = - 0.0013 H^2 + 0.0967 H + 0.7789 (R^2 = 0.53, F =
495 7.72, p = 0.002, n = 12)] explains 53% variability between dependent & independent variables
496 indicating significant influence of sensible heat flux on variability of biosphere – atmosphere CH_4
497 exchange in this tropical mangrove forest ecosystem.

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498 On annual basis mean daytime CH_4 mixing ratio was 1.03 times lower than night-time; the variability is
499 presumed to be governed by photo-oxidation and diurnal changes in the boundary layer height. But
500 statistically no significant correlation was obtained between variability of daytime and nighttime CH_4
501 mixing ratio with PBL height (ΔCH_4 = - 0.0118ΔPBL + 0.3045, R^2 = 16.2%, F = 0.321, p = 0.987, n =
502 12); indicating variability of atmospheric boundary layer height was not the major controlling factor for
503 ΔCH_4, that pointed towards large atmospheric CH_4 photo-oxidation in the mangrove forest atmosphere.
504 CH_4 photo-oxidation rate in this subtropical mangrove forest atmosphere varied between 6.05 x 10^{10} and
505 1.67 x 10^{11} molecules cm^{-3} d^{-1} being maximum oxidation during monsoon and minimum during
506 postmonsoon periods (Dutta et al. 2015c). The peak monsoon CH_4 photo-oxidation rate may be
507 attributed to maximum CH_4 supply through emission as well as high UV index and UV erythermal dose
508 irradiance during this period in these subtropical latitudes (Panicker et al. 2014). Considering the mean
509 day light period as 12 hours and 6.023 x 10^{23} molecules equals to 1 mole or 16000 mg CH_4, the mean
510 CH_4 photo-oxidation rate in this tropical mangrove forest atmosphere was calculated as 3.25 x 10^{-9} mg
511 cm^{-3} d^{-1}.

512 **4.4: Quantitative CH_4 budget from Indian Sundarbans:**

513 A box diagram (fig.9) was constructed for describing biogeochemical CH_4 cycling in Sundarbans
514 biosphere reserve. In the model different subsystems are designated as separate reservoir. CH_4 storage in
515 each reservoir and exchange fluxes of CH_4 between different reservoirs are presented as an annual mean

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516 and values were used to calculate the input and output of CH_4 to/from the reservoirs, which in turn
517 established the CH_4 budget for this mangrove-dominated estuarine system.

518 **Mangrove sediment methane budget:**

519 1. Mean CH_4 production potential in intertidal forest sediment (up to the depth of 25 cm) was 3547
520 µmol m^{-3} d^{-1}. Considering the rate equal to in situ CH_4 production and extrapolating over entire
521 forest, total CH_4 production within 25 cm depth of the forest sediment is 21.75 $Ggyr^{-1}$.

522 2. Intertidal sediment pore water CH_4 concentration was 3451 nM and extrapolating the
523 concentration for entire mangrove forest (up to 25 cm depth), the sediment stands as a reservoir
524 pool of 0.031Gg CH_4.

525 3. The intertidal sediment pore water methane concentration was about 55 times supersaturated
526 than adjacent estuarine water (63.04 nM) indicating significant out - flux of CH_4 rich pore water
527 from intertidal sediment to estuary during low tide phase via advective transport.

528 4. About 8.2% of the produced CH_4 is advectively transported to the adjacent estuarine system with
529 a rate of 159.52 µmol m^{-2} d^{-1}.

530 5. Mean CH_4 oxidation potential at intertidal forest sediment surface was 1.758 mg m^{-2} d^{-1} and
531 total oxidation was 2.70 $Ggyr^{-1}$, when extrapolated for entire forest area of Sundarbans. The

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532 value indicates only 12.41% of produced CH_4 is oxidized at sediment surface; presenting petite
533 activity of methanotrophs in comparison to the methanogens in forest sediment.

534 6. Total CH_4 emission across sediment – atmosphere interface of the mangrove forest was 10.8
535 $Ggyr^{-1}$ (about 49.6% of total produced CH_4 in sediment) with a rate of 7.06 mg m^{-2} d^{-1}.

536 7. The total CH_4 emission and oxidation from/at the mangrove surface sediment was 6.05 and 1.51
537 times higher, respectively compare to total CH_4 advectively transported to the estuary; indicates
538 emission acts as major CH_4 removal pathway from intertidal mangrove sediment.

539 8. Balancing total production and removal, annually 6.46 $GgCH_4$ remains unexplained. This
540 establishes the existence of anaerobic methane oxidation in mangrove sediment column which
541 was not covered in this study.

542 **Sub-tidal sediment CH_4 budget:**

543 **1.** CH_4 production potential of 0 – 5 cm depth of estuarine underlying sediment (sub-tidal
544 sediment) was 48.88 µmol m^{-3} d^{-1} and total production was 0.026 $Ggyr^{-1}$ when extrapolated for
545 entire sub-tidal area for estuaries of Sundarbans.

546 **2.** Mean sub-tidal sediment (0 – 5 cm) pore water CH_4 concentration was 3286 nM; which was
547 about 52.13 times supersaturated than overlying estuarine water inducing diffusive CH_4 transport
548 from sub-tidal sediment to the overlying estuary.

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549 **3.** Mean diffusive CH_4 flux from sub-tidal sediment to the overlying estuary was 8.45 µmol m^{-2} d^{-1}.
550 Extrapolating the rate for entire sub-tidal area of Sundarbans, the sub-tidal sediment acts as a
551 source of 0.089 GgCH_4 annually to the upper estuarine system.

552 **Estuarine CH_4 budget:**

553 1. Total CH_4 input from sediment to estuary (by both advection and diffusion transports) was
554 1.875Gg yr^{-1}. Advective flux being 20 times higher than diffusive flux acts as major source for
555 CH_4 to the estuary.

556 2. Mean dissolved CH_4 concentration in the estuary was 63.04 nM. Extrapolating this over the
557 entire volume of the estuaries of the Sundarbans, the system stands as a reserve pool of 0.011Gg
558 CH_4 (Dutta et al., 2015b).

559 3. The total CH_4 oxidation rate in the estuarine water column was 1.30Ggyr^{-1} with a rate of 20.59
560 nmol L^{-1} d^{-1}.

561 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
563 associated estuaries of the Sundarbans are a source of 0.093Gg CH_4 to the regional atmosphere,
564 which is only 4.96 % of total CH_4 supplied to the estuary.

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5. CH_4 oxidation, being 14 times higher than water - atmosphere exchange, is considered as principal CH_4 removal mechanism in this estuary.

6. Mean turnover time of CH_4 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 CH_4 due to these oxidation and emission processes were 1.39 $Ggyr^{-1}$, about 74.13 % of total CH_4 supply to the estuary, indicating a significant export flux of CH_4 from estuary to the adjacent continental shelf.

8. Balancing CH_4 sources vs. sinks in this estuarine system, the export flux of CH_4 from estuary to the continental shelf was 0.485 $Ggyr^{-1}$, indicating a significant contribution from the Sundarbans estuaries to the CH_4 budget of the northern Bay of Bengal (Dutta et al., 2015b).

Atmospheric CH_4 budget:

1. Net CH_4 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 CH_4 emission rate from mangrove forest & creeks (10.76 mg m^{-2} d^{-1}; Barnes et al., 2006) mean CH_4 emission rate from Sundarbans mangrove environment is

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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_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 $GgCH_4$.
4. The annual mean mangrove biosphere atmosphere CH_4 exchange flux was 0.086 mg m^{-2} d^{-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 $GgCH_4$ to the regional atmosphere (about 2.75% of total CH_4 input from water & sediment surfaces).
5. Total CH_4 photo-oxidation in the forest atmosphere up to height of atmospheric boundary layer was 9.26 $Ggyr^{-1}$ with a mean rate of 3.25 x 10^{-9} mg cm^{-3} d^{-1}. Compare to total CH_4 supply to the forest atmosphere, about 85% is photo-oxidized within atmospheric boundary layer of Sundarbans and is recognized as major atmospheric CH_4 removal pathway. The photo-oxidation mediated depletion of CH_4 is highly significant in atmospheric chemistry producing byproducts like HCHO, O_3 depending upon ambient NO_x level. Balancing total atmospheric sources and sinks, annually 1.33Gg CH_4 remains unbalanced in the atmosphere, which enriches regional atmospheric CH_4 mixing ratio.

5. Conclusion:

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600 CH_4 production potential within 25 cm depth of the forest sediment is 21.75 $Ggyr^{-1}$ and pore water CH_4
601 concentration was 3541 nM. CH_4 fluxes across intertidal sediment – atmosphere interface acts as major
602 sink for produced CH_4 in intertidal sediment over surface layer CH_4 oxidation and advective CH_4
603 transport to estuary. The process of methanogenesis is totally restricted within estuarine water column
604 and is supplied from adjacent mangrove forest ecosystem and underlying sediment of the estuary.
605 Advective flux being 20 times higher than diffusive flux acts as major source for CH_4 to the estuary.
606 CH_4 oxidation, being 14 times higher than water - atmosphere exchange, is considered the principal
607 CH_4 removal mechanism in this estuary. Total annual CH_4 emission from sediment and water surfaces
608 of the Sundarbans mangrove biosphere was 10.89Gg, of which sediment is the principal contributor
609 (99.17%). Compare to total CH_4 supply to the atmosphere, about 85% is photo-oxidized within
610 atmospheric boundary layer of Sundarbans and 2.75% is transported to the upper atmosphere through
611 biosphere – atmosphere CH_4 exchange flux.

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758 **Table 1: Seasonal variation of CH_4 production potential and pore water CH_4 concentrations in**
759 **intertidal and sub-tidal sediments. Here, T = soil surface temperature; S = pore water salinity;**
760 **$[CH_4]_{(PI)}$ = CH_4 production potential in intertidal sediment; IS = intertidal sediment; SS = sub-**
761 **tidal sediment.**

Season	T (^oC)	S	Depth (cm)	$[CH_4]_{(PI)}$ ($\mu mol\ m^{-3}\ d^{-1}$)	$[CH_4]_{(IS)}$ (μM)	$[CH_4]_{(SS)}$ (μM)
Premonsoon	28.36 ±1.02	28.88 ± 0.13	0 – 5	ND	2292	2770 ± 1039
			5 – 10	214.99	2313	
			10 – 15	2088.67	2334	
			15 – 20	2918.89	3804	
			20 - 25	4290.22	5274	
Monsoon	28.01 ± 0.41	22.55 ± 0.31	0 – 5	ND	1881	3110 ± 1023
			5 – 10	823.58	2155	
			10 – 15	3539.90	2429	
			15 – 20	4373.44	4508	
			20 - 25	5850.478	6587	
Postmonsoon	18.25 ± 0.22	25.98 ± 0.45	0 – 5	ND	2246	3980 ± 1227
			5 – 10	1175.56	2319	
			10 – 15	4033.30	2413	
			15 – 20	5903.10	4542	
			20 - 25	7352.94	6670	

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762 **Table 2: Results of multiple regression analysis between pore water CH_4 concentrations, E_h, NO_2^-,**

763 **SO_4^{2-}, AVS and organic carbon (OC) concentration.**

Predictor	Coef	SE Coef	T	P
Constant	10.601	2.921	3.63	0.005
E_h	-0.018447	0.009074	-2.03	0.013
NO_2^-	-0.12277	0.05477	-2.24	0.052
SO_4^{2-}	- 0.00764	0.01454	-0.53	0.612
AVS	- 0.06933	0.04129	-1.68	0.127
%OC	- 4.086	1.086	-3.76	0.004

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769 **Table 3: Results of multiple regression analysis between surface layer CH_4 oxidation potential**

770 **($[CH_4]_{(ox)}$) vs. NH_4^+ & NO_3^- concentrations .**

Predictor	Coef	SE Coef	T	*P*
Constant	1.6338	0.3253	5.02	0.015
NH_4^+	-0.3065	0.1362	-2.25	0.110
NO_3^-	0.2930	0.1285	2.28	0.107

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779 **Table 4: Seasonal variation of dissolved CH_4 concentrations, physicochemical and biological**
780 **parameters of estuarine water.**

Properties	Parameters	Position	Premonsoon	Monsoon	Postmonsoon
	$[CH_4]$ (nM)	Surface	54.20 ± 5.06	64.58 ± 10.56	90.91 ± 21.20
		Bottom	47.28 ± 12.85	53.27±19.47	67.97 ± 33.12
Physical property	Temperature (°C)	Surface	29.99 ± 0.97	27.82 ± 0.26	19.88 ± 0.18
		Bottom	28.79 ± 0.07	26.92 ± 0.62	19.08 ± 0.78
	S_D (cm)		62.3 ± 13.1	29.7 ± 7.8	75.9 ± 7.7
Chemical properties	Salinity	Surface	27.09 ± 0.59	19.06 ± 4.33	22.33 ± 0.81
		Bottom	26.88 ± 0.15	18.87 ± 0.33	22.14 ± 0.65
	DO (mg L^{-1})	Surface	6.53 ± 0.29	6.04 ± 0.73	7.27 ± 1.14
		Bottom	5.83 ± 0.37	5.41 ± 0.03	5.98 ± 0.79
	pH	Surface	8.17 ± 0.16	8.10 ± 0.03	8.15 ± 0.06
Biological properties	Chl (μg L^{-1})	Surface	5.30 ± 0.19	3.11 ± 0.39	7.88 ± 1.90
	P (mg C m^{-2} hr^{-1})	Surface	56.9 ± 7.1	48.2 ± 8.0	88.0 ± 18.6
	R (mg C m^{-2} hr^{-1})	Surface	125.0 ± 100	102.8 ± 116.7	110.1 ± 65.6

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784 **Table 5: Results of multiple regression analysis between [CH_4] and temperature (T) (^oC), pH,**
785 **chlorophyll (Chl) (µg L^{-1}), dissolved oxygen (DO) (mg L^{-1}), productivity and community**
786 **respiration ratio (P / R).**

Predictor	Coef	SE Coef	T	P
Constant	-296.8	986.5	-0.30	0.792
T	-0.140	2.178	-0.06	0.955
pH	57.6	103.1	0.56	0.633
Chl	2.688	5.801	0.46	0.689
DO	-19.13	28.82	-0.66	0.575
P / R	8.50	61.86	0.14	0.903

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792 **Table 6: Results of multiple regression analysis between dissolved methane consumption rate**
793 **($[CH_4]_{DOX}$) vs. water temperature (T), salinity (S), dissolved oxygen (DO), DIN, net heterotrophy**
794 **(P/R) and secchi disc depth (S_d).**

Predictor	Coef	SE Coef	T	*P*
Constant	-65.85	22.24	-2.96	0.031
T	0.7561	0.6142	1.23	0.273
S	2.1752	0.4949	4.40	0.007
DO	7.528	2.868	2.62	0.047
DIN	-0.4082	0.3686	-1.11	0.318
P/R	-2.012	2.938	-0.68	0.524
S_d	-0.30365	0.09738	-3.12	0.026

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Table 7: Seasonal variation of micrometeorological parameters, methane mixing ratio, biosphere – atmosphere CH_4 exchange and CH_4 photo-oxidation in mangrove forest atmosphere.

Parameters	Height(m)	Premonsoon	Monsoon	Postmonsoon
Air temp. (^oC)	10	30.34 ± 0.91	29.74 ± 2.50	17.34 ± 4.09
	20	29.73 ± 1.13	28.37 ± 0.88	16.17 ± 1.80
Wind velocity(ms^{-1})	10	0.70 ± 0.42	1.32 ± 1.11	0.41 ± 0.36
	20	0.95 ± 0.44	1.64 ± 1.37	0.80 ± 0.88
U* (m/sec)		0.20 ± 0.04	0.15 ± 0.15	0.17 ± 0.49
Z_o (m)		3.77 ± 3.01	1.63 ± 1.02	2.97 ± 2.98
$C_{D(10m)}$		0.386	0.157	0.167
H ($W\ m^{-2}$)		6.349	8.248	1.154
PBL (m)		936.59	702.45	796.10
CH_4 (ppmv)	10	1.769 ± 0.04	2.180 ± 0.12	2.112 ± 0.05
	20	1.821 ± 0.09	2.027 ± 0.03	2.116 ± 0.06
F_{BA} ($mg\ m^{-2}\ hr^{-1}$)		- 4.514	6.635	-2.110
$[CH_4]_{photo\text{-}ox\ rate}$ ($molecules\ cm^{-3}\ d^{-1}$)	10	1.40×10^{11}	1.67×10^{11}	6.05×10^{10}

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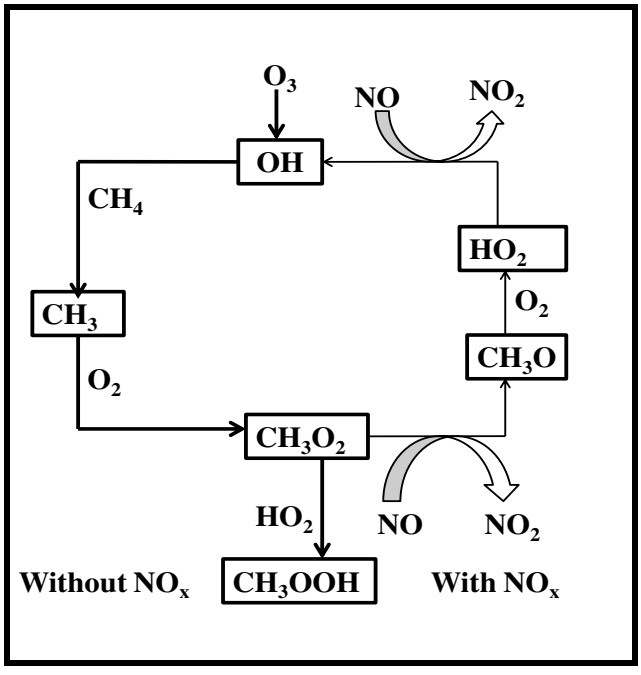

Fig.1: Schematic diagram of atmospheric CH_4 photooxidation with/without NO_x concentration.

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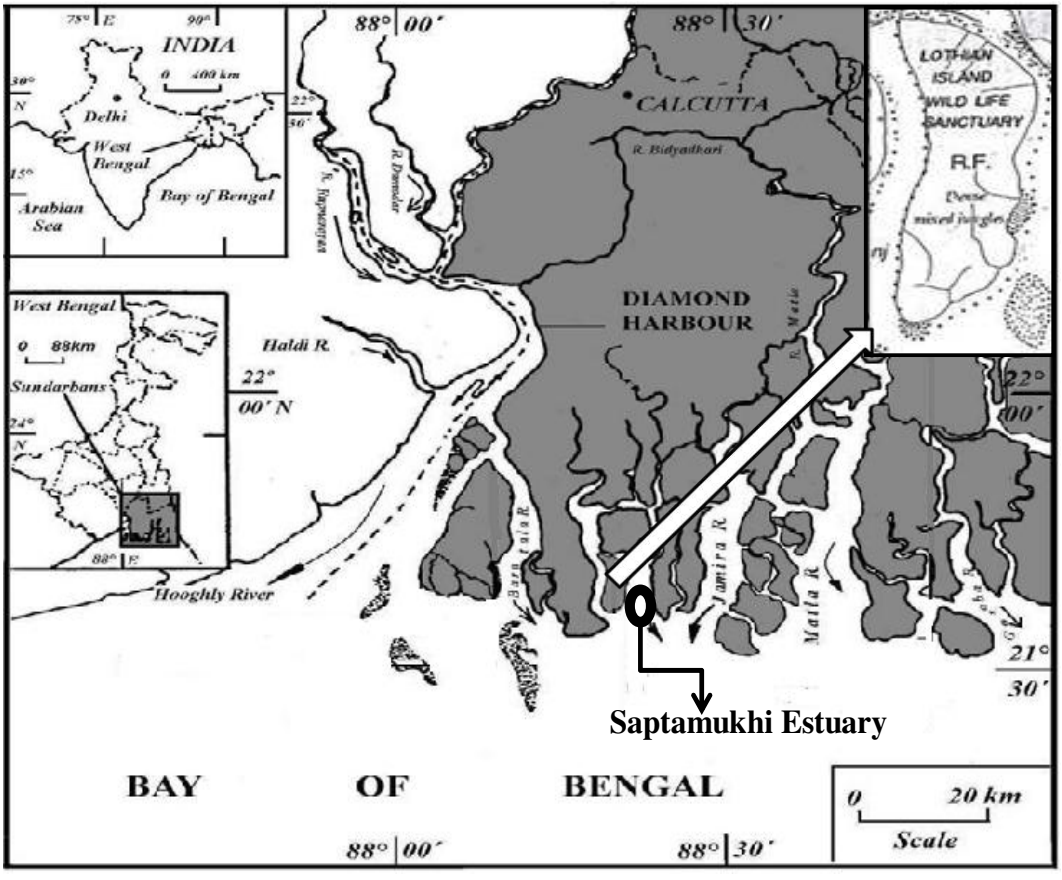

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805 Fig.2: Map showing locations of the study point.

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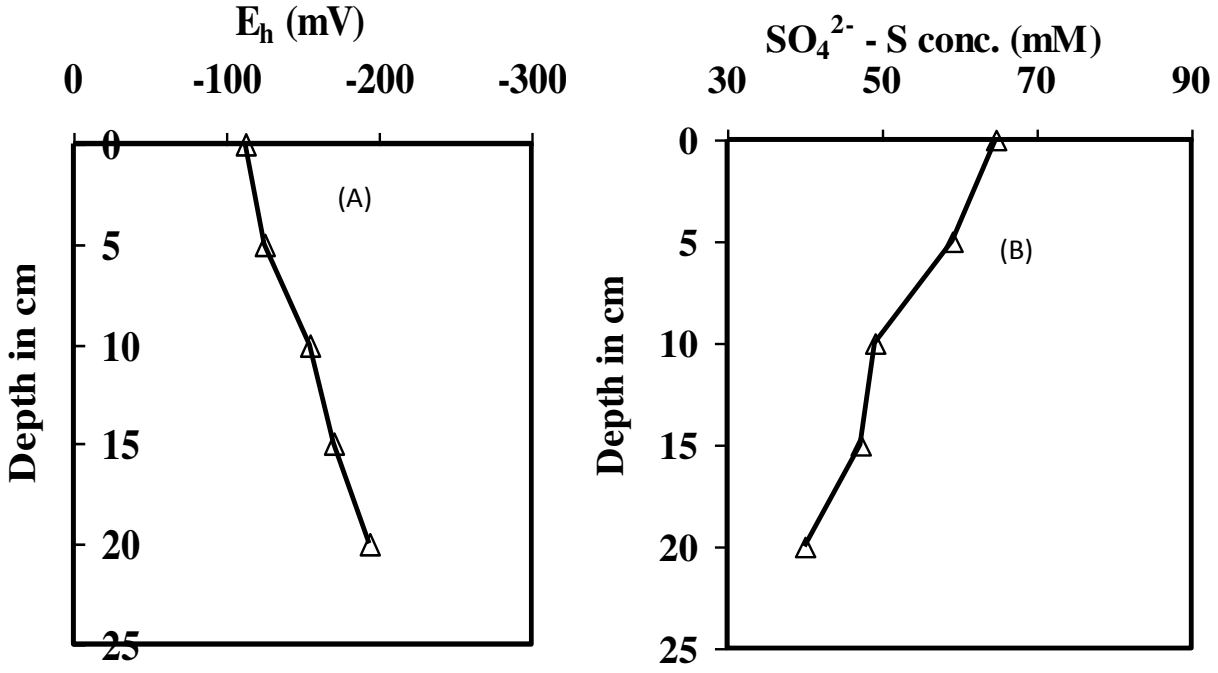

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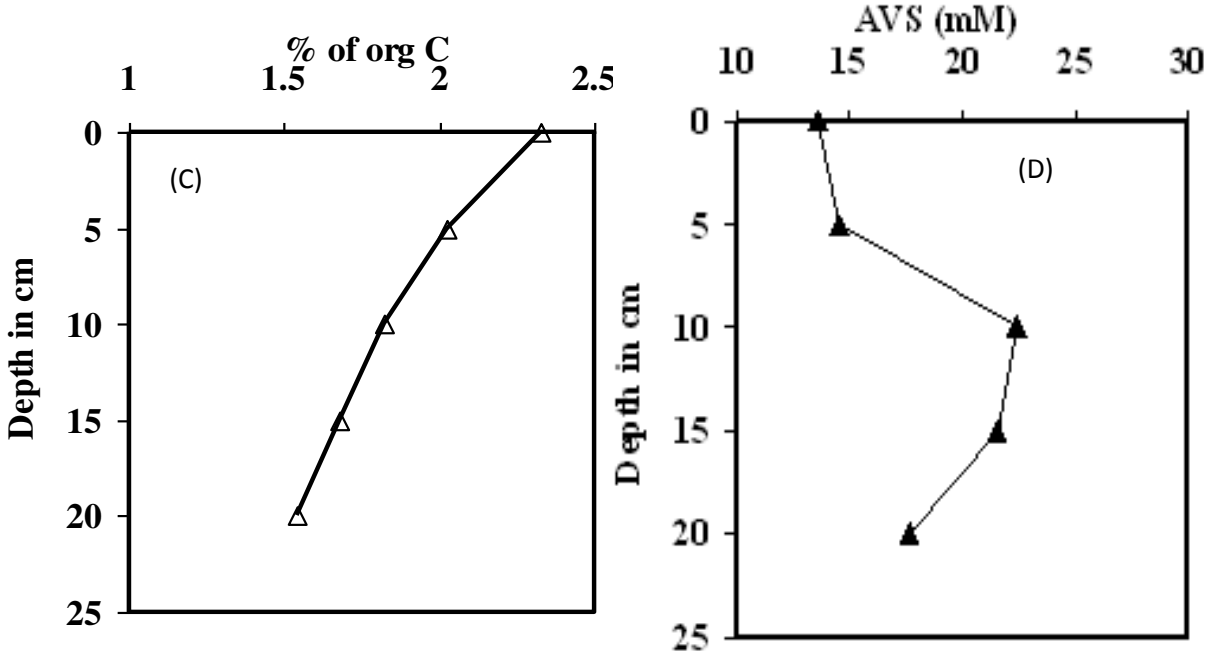

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808 Fig.3: Vertical variation of physicochemical properties of mangrove sediment (A) E_h (B) pore water
809 sulphate – S concentration (C) % organic carbon (D) pore water AVS concentration

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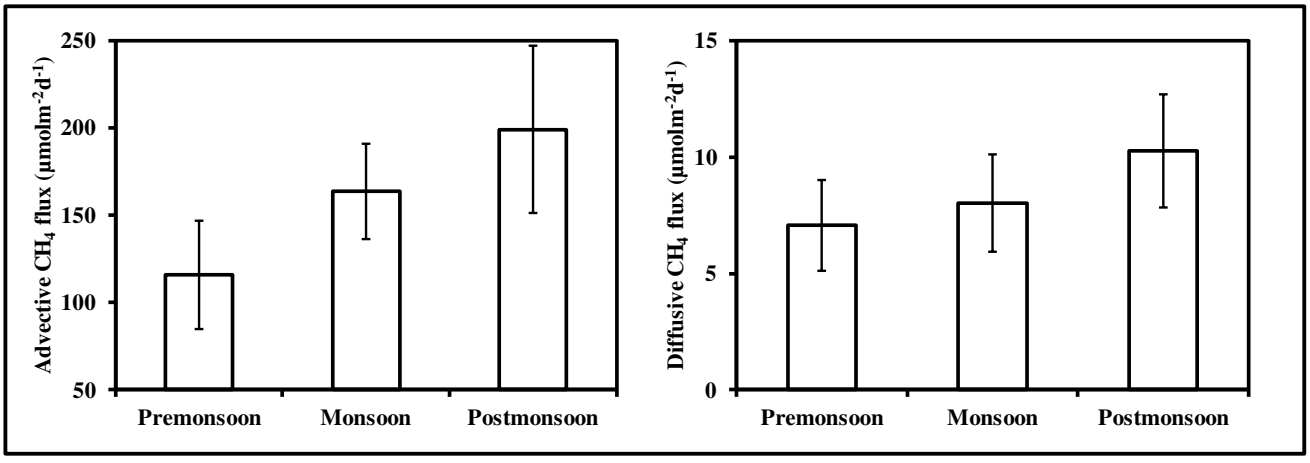

Fig.4: Seasonal variation of advective and diffusive CH_4 fluxes from intertidal and subtidal sediments, respectively.

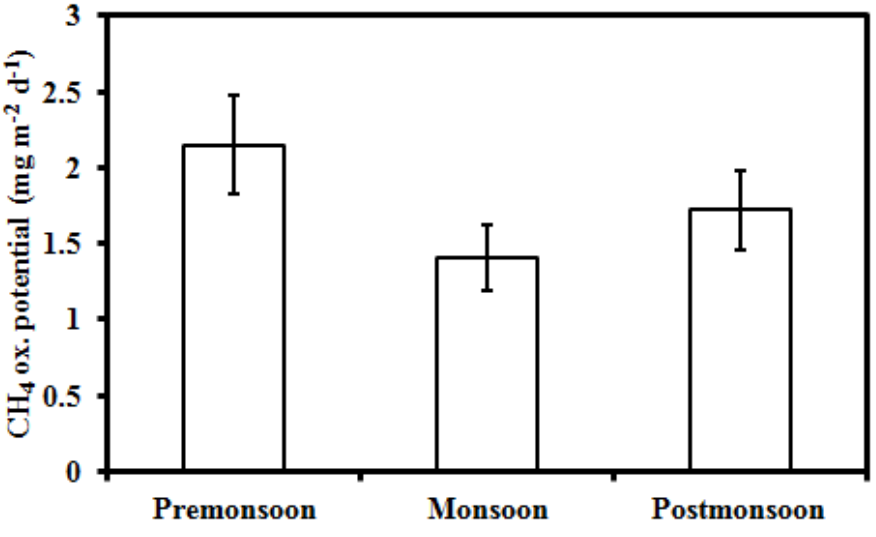

Fig.5: Seasonal variations of surface sediment CH_4 oxidation potential in mangrove sediment.

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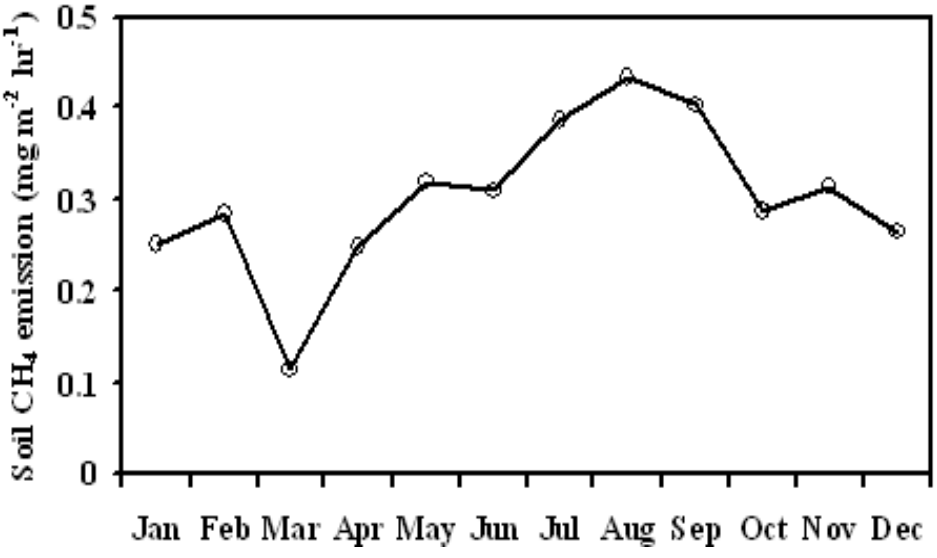

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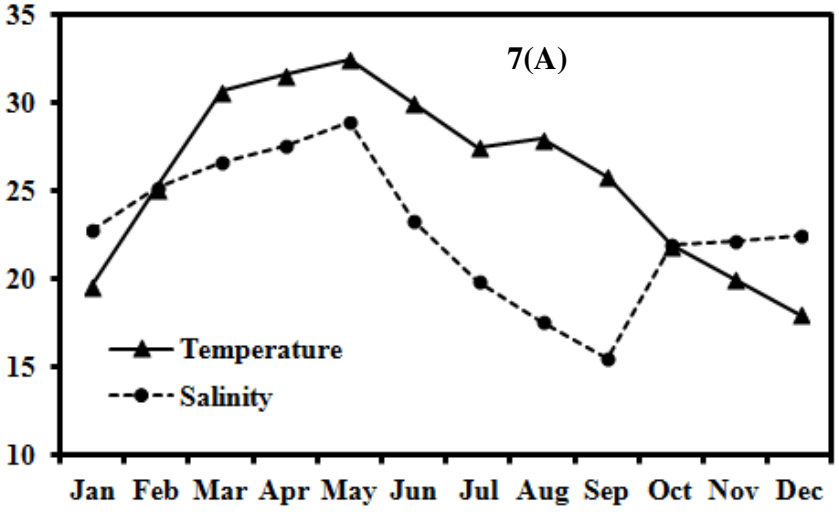
816 Fig.6: Monthly variation of soil methane emission from intertidal mangrove forest.



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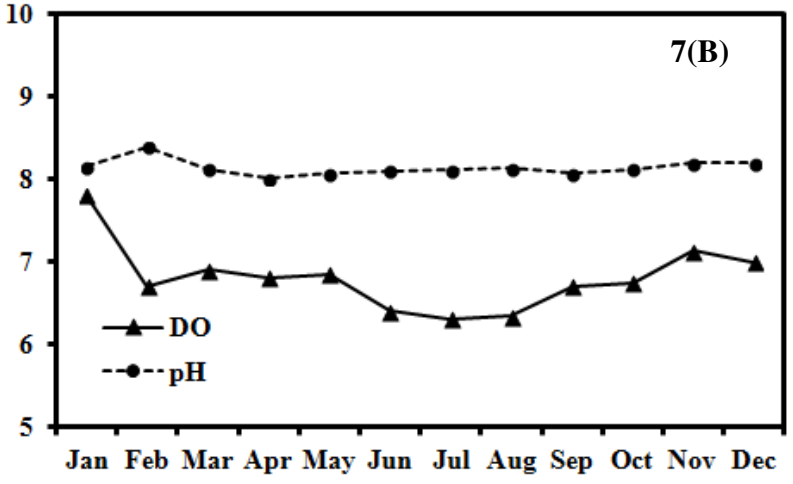

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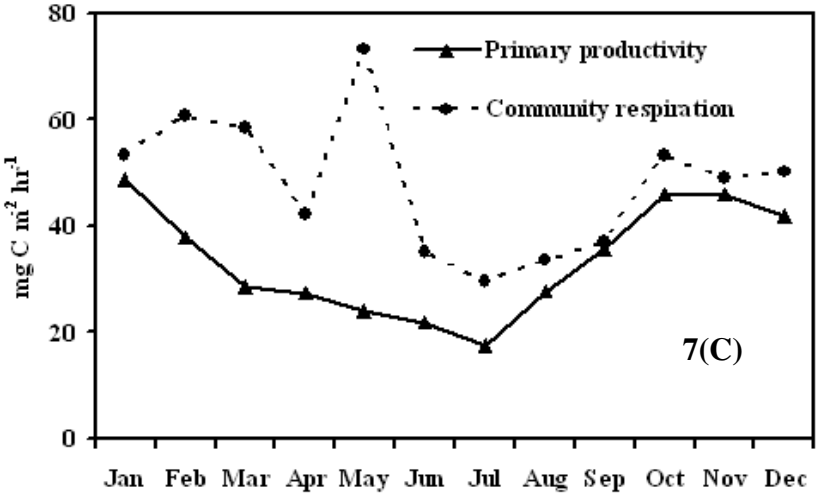

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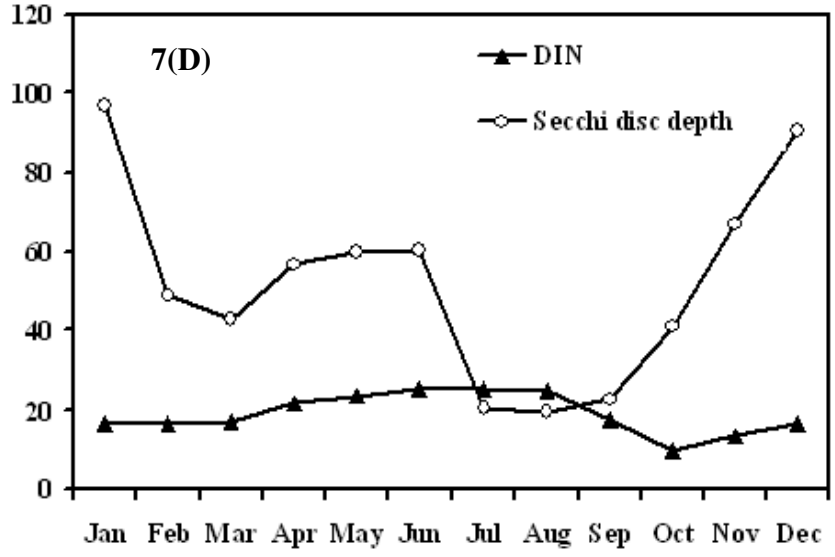

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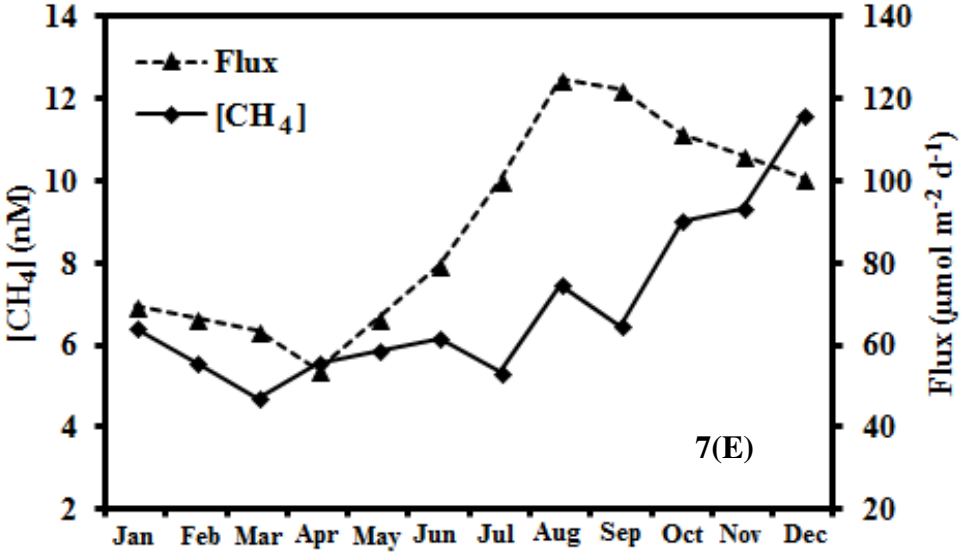

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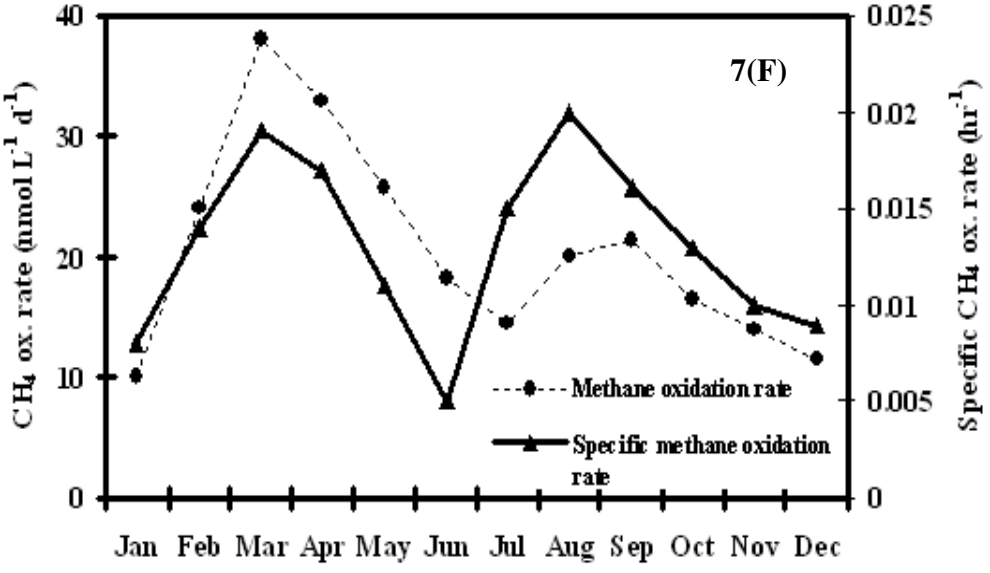

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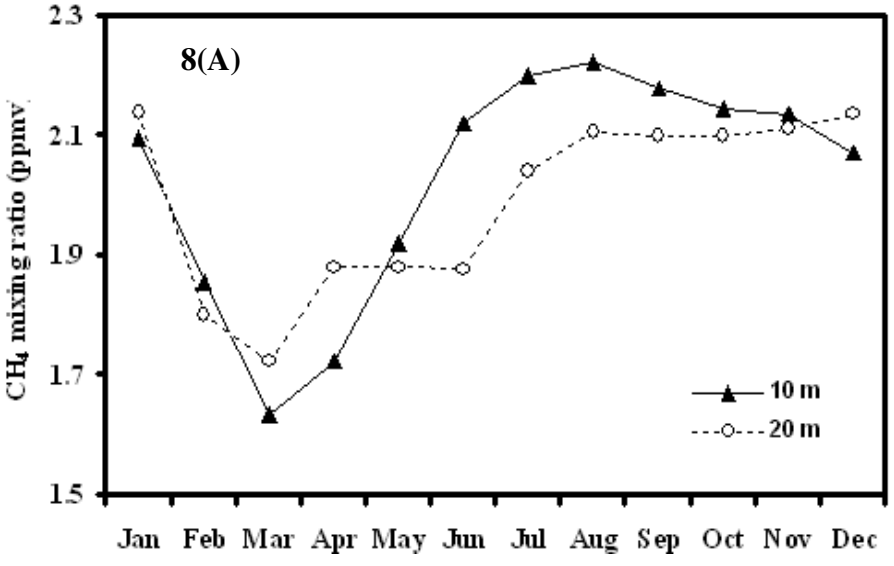
828 Fig.7: Monthly variation of physicochemical parameters along with dissolved methane concentrations,

829 methane oxidation and air-water methane exchange flux.



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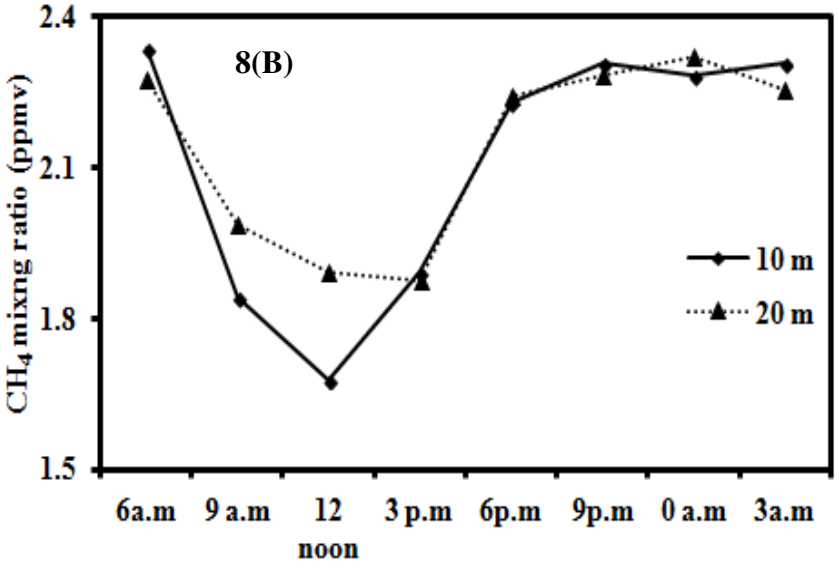

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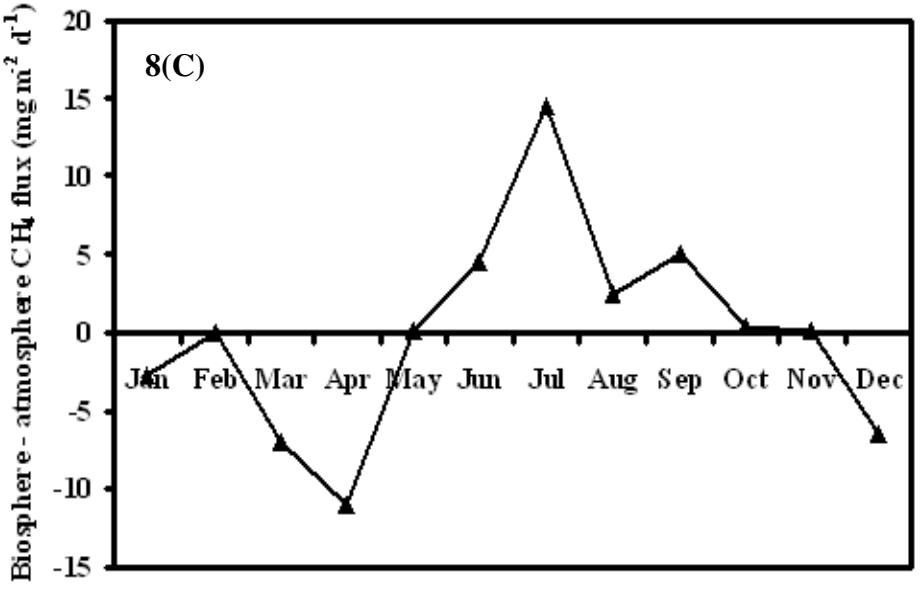

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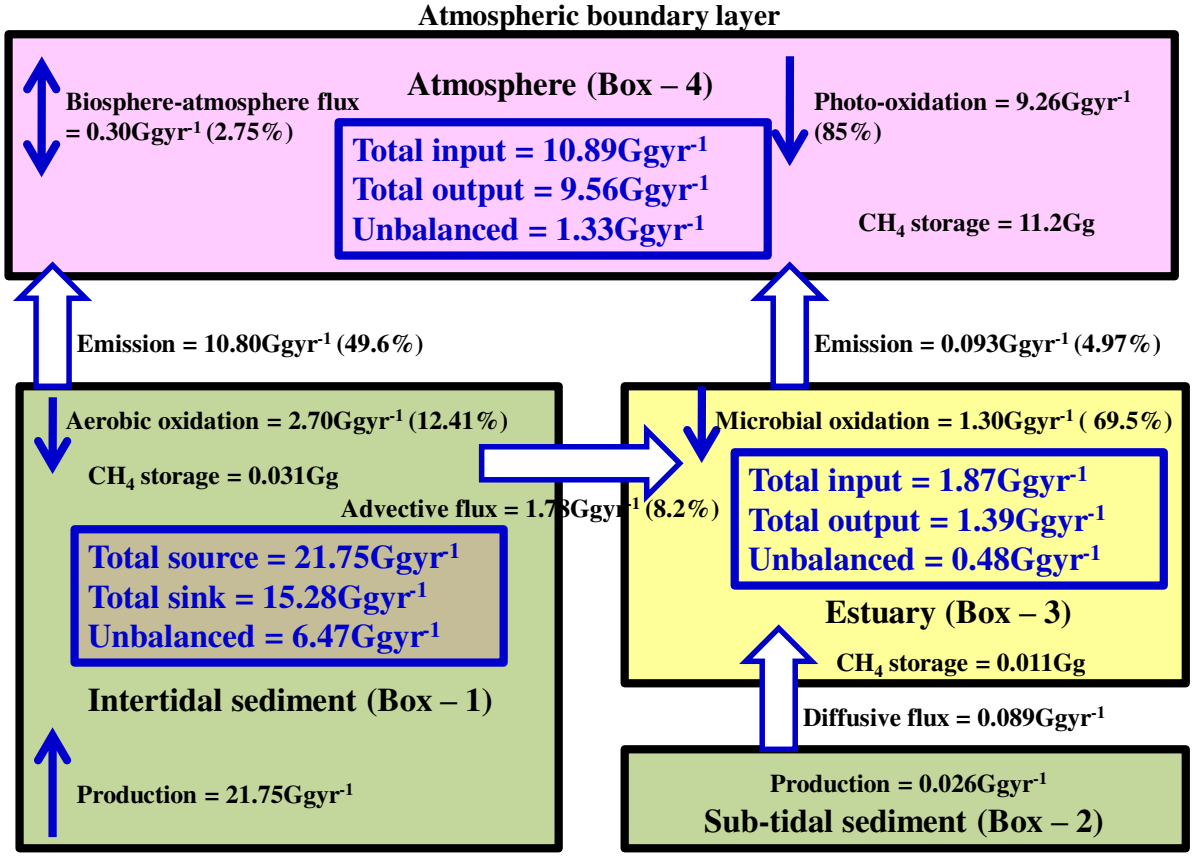
833 Fig.8: (A) Monthly variation of methane mixing ratio in forest atmosphere (B) Diurnal variation of
834 methane mixing ratio in forest atmosphere (C) Monthly variation of biosphere-atmosphere methane
835 exchange flux.



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

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