Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


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

**Manab Kumar Dutta[1*], Sandip Kumar Mukhopadhyay[2]**

[1]Geoscience Division, Physical Research Laboratory, Ahmedabad – 380009, India

[2]Department of Marine Science, University of Calcutta. 35, Ballygunge Circular Road, Kolkata - 700019, West Bengal, India

***Author for correspondence**: Postdoctoral Fellow. Geoscience Division, Physical Research Laboratory, Ahmedabad – 380009, India. Email: manabdutta.1987@gmail.com

**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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 $km^2$ 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 $km^2$. 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 –

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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^o$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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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, $\Phi$ =
153 porosity of sediment = 0.58 (Dutta et al. 2013), $\nu$ = 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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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, $\Delta C$ 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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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).

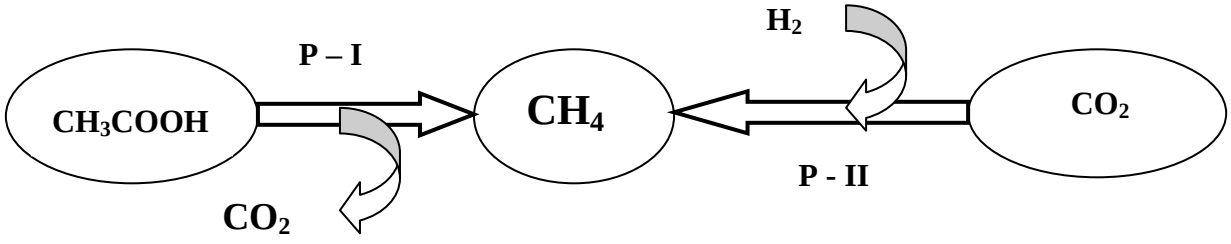
$CH_4$ production potential of first 5 cm deep sub-tidal sediment layer varied between 18.72 – 85.74 µmol $m^{-3}d^{-1}$ having maximal (77.06 ± 12.27 µmol $m^{-3}$ $d^{-1}$) postmonsoon and minimal (21.28 ± 3.63 µmol $m^{-3}$ $d^{-1}$) premonsoon. Mean methanogenesis rate of sub-tidal sediment (0 – 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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 =

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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).

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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$^oC$ 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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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:**

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 $L^{-1}$ $d^{-}$
390 $^{1}$) (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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




DIN conditions (< 3µM). The nitrogen fixation is disrupted by high concentrations of $O_2$ 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 $CH_4$ levels in estuarine water column (Abil et al. 2007).

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

In a study of $CH_4$ oxidation in a freshwater lake, Panganiban et al. 1979 reported that 30-60% of the $CH_4$ 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 $CH_4$ oxidation in a freshwater lake. In the mangrove dominated estuary of Sundarbans, the $CH_4$ oxidation in the water column progressed at aerobic conditions. Assuming that 30-50% of the $CH_4$ carbon oxidized by methanotrophs was converted to organic matter (bacterial cell materials) and the remainder to $CO_2$. The mean $CH_4$ carbon converted to bacterial cell material was

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 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$^oC$ at 10 m and 16.17 ± 1.80 to 29.73 ± 1.13$^oC$ 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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 ($\Delta CH_4$ = - 0.0118$\Delta$PBL + 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 $\Delta CH_4$, 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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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:

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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.

612 **6. Acknowledgement:**

613 The authors thank the Ministry of Earth Science, Govt. of India sponsored Sustained Indian Ocean
614 Biogeochemistry and Ecological Research (SIBER) proggrame for partial financial support to carry out
615 the study. We are thankful to the Sundarbans Biosphere Reserve for extending necessary help and
616 support for conducting fieldwork and measurements related to the study.

617 **7. References:**

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


618 Abril, G., Commarieu, M.V., Gue´rin, F.: Enhanced methane oxidation in an estuarine turbidity
619 maximum. Limnol. Oceanogr. 52(1), 470 – 475, 2007.

620 Barnes, J., Ramesh, R., Purvaja, R., Nirmal Rajkumar, A., Senthil Kumar, B., Krithika, K.,
621 Ravichandran, K., Uher, G., Upstill-Goddard, R.: Tidal dynamics and rainfall control $N_2O$ and $CH_4$
622 emissions from a pristine mangrove creek. Geophys. Res. Lett. 33, L15405, 2006.

623 Barrett K.: Oceanic ammonia emissions in Europe and their transboundary fluxes. Atmospheric
624 Environment 32, 381 – 391, 1998.

625 Bartlett, K. B., Bartlett, D. S., Harris, R. C., Sebacher, D. I.: Methane emissions along a salt marsh
626 gradient. Biogeochemistry 4, 183-202, 1987.

627 Be'dard, C., Knowles, R., 1989. Physiology, biochemistry, and specific inhibitors of $CH_4$, $NH_4^+$, and
628 CO oxidation by methanotrophs and nitrifiers. Microbiol. Rev. 53, 68–84.

629 Biswas, H., Mukhopadhyay, S.K., Sen, S., Jana, T.K.: Spatial and temporal patterns of methane
630 dynamics in the tropical mangrove dominated estuary, NE Coast of Bay of Bengal, India. . J. Mar. Syst.
631 68, 55–64, 2007.

632 Bouillon, S., Middelburg, J.J., Dehairs, F., Borges, A.V., Abril, G., Flindt, M.R., Ulomi, S., Kristensen,
633 E.: Importance of intertidal sediment processes and porewater exchange on the water column
634 biogeochemistry in a pristine mangrove creek (Ras Dege, Tanzania). Biogeosciences 4, 311-322, 2007c.

635 Bradford, M.A., Ineson, P., Wookey, P.A., Lappin-Scott, H.M.: The effects of acid nitrogen and acid
636 sulphur deposition on $CH_4$ oxidation in a forest soil: a laboratory study. Soil Biol Biochem 33,1695 –
637 1702, 2001b.
638 Canfield, D. E., Kristensen, E., Thamdrup, B.O.: The sulfur cycle. Advanced Marine Biology 48, 313 –
639 381, 2005.

640 De Angelis, M.A., Scranton, M.I.: Fate of methane in the Hudson River and estuary. Glob.
641 Biogeochem. Cycles 7, 509 –523, 1993.

642 De Angelis, M.A., Lilley, M.D.: Methane in surface waters of Oregon estuaries and rivers. Limnol.
643 Oceanogr. 32, 716 –722, 1987.

644 Dutta, M.K, Ray, R., Mukherjee, R., Jana, T.K., Mukhopadhyay, S.K.: Atmospheric fluxes and photo-
645 oxidation of methane in the mangrove environment of the Sundarbans, NE coast of India; A case study
646 from Lothian Island. Agricultural and Forest Meteorology, 213, 33 – 41, 2015c.

647 Dutta, M.K., Mukherkjee, R., Jana, T.K., Mukhopadhyay, S.K.: Biogeochemical dynamics of
648 exogenous methane in an estuary associated to a mangrove biosphere; the Sundarbans, NE coast of
649 India. Marine Chemistry 170, 1 – 10, 2015b.

650 Dutta, M.K., Chowdhury, C., Jana, T.K., Mukhopadhyay, S.K.: Dynamics and exchange fluxes of
651 methane in the estuarine mangrove environment of Sundarbans, NE coast of India. Atmos. Environ. 77,
652 631-639, 2013.

653 Ding, W., Cai, Z., Tsuruta, H., Li, X.: Key factors affecting spatial variation of methane emissions
654 from freshwater marshes. Chemosphere 51, 167–173, 2003.

655 Ehhalt D.H., Rohrer, F.: Dependence of the OH concentration on solar UV. Journal of Geophysical
656 Research, 105, 3565-3571, 2009.

657 Frankignoulle, M., Borges, A.V.: Direct and indirect pCO2 measurements in a wide range of pCO2 and
658 salinity values (the Scheldt estuary), Aquat. Geochem. 7, 267–273, 2001.

659 Ganguly D., Dey, M., Mandal, S.K., De, T.K., Jana, T.K.: Energy dynamics and its implication to
660 biosphere-atmosphere exchange of $CO_2$, $H_2O$ and $CH_4$ in a tropical mangrove forest canopy.
661 Atmospheric Environment, 42, 4172 – 4184, 2008.

662 Grasshoff, K., Ehrharft, M., Kremling, K.: Methods of seawater analysis, 2nd edition. Germany, 1983.

663 Hanson, R.S., Hanson, T.E.: Methanotrophic bacteria. Micro. and Mole. Bio. Rev. 60, 439-471, 1996.

664 Hoehler, T.M., Alperin, M.J.: Biogeochemistry: Methane minimalism. Nature 507, 436 – 437, 2014.

665 IPCC, 2007. Summary for policymakers. In: Solomon, S., et al. (Ed.), Climate Change
666 2007: the Physical Science Basis. Contribution of Working Group I to the Fourth Assessment
667 Report of the Intergovernmental Panel on Climate Change. Cambridge University
668 Press, Cambridge.

669 Jang, I., Lee, S., Hong, J., Kang, H.: Methane oxidation rates in forest soils and their controlling
670 variables: a review and a case study in Korea. Ecol Res, 21, 849–854, 2006.

671 Kankaala, P., Huotari, J., Peltomaa, E., Saloranta, T., Ojala, A.: Methanotrophic activity in relation to
672 methane efflux and total heterotrophic bacterial production in a stratified, humic, boreal lake. Limnol.
673 Oceanogr. 51, 1195–1204, 2006.

674 Kelley, C.A., Martens, C.S., Chanton, J.P.: Variations in sedimentary carbon remineralization rates in
675 the White Oak River estuary, North Carolina. Limnol. Oceanogr. 35, 372–383, 1990.

676 Keller, J. K., Takagi, K. K.: Solid-phase organic matter reduction regulates anaerobic decomposition in
677 bog soil. Ecosphere, 4, 54, 2003.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


678 Knab, N. J., Cragg, B.A., Hornibrook, E.R.C., Holmkvist, L., Pancost, R.D., Borowski, C., Parkes, R.J.,
679 Jørgensen, B.B.: Regulation of anaerobic methane oxidation in sediments of the Black Sea.
680 Biogeosciences, 6, 1505–1518, 2009.

681 Kristensen, E., Flindt, M.R., Ulomi, S., Borges, A.V., Abril, G., Bouillon, S.: Emission of $CO_2$ and $CH_4$
682 to the atmosphere by sediments and open waters in two Tanzanian mangrove forests. Mar. Ecol. Prog.
683 Ser. 370, 53–67, 2008.

684 Kristensen, E., Alongi, D.M.: Control by fiddler crabs (Uca vocans) and plant roots (Avicennia marina)
685 on carbon, iron, and sulfur biogeochemistry in mangrove sediment. Limnology and Oceanography,
686 51(4), 1557–1571, 2006.

687 Lekphet, S., Nitisoravut, S., Adsavakulchai, S.: Estimating methane emissions from mangrove area in
688 Ranong Province, Thailand. Songklanakarin J. Sci. Technol., 27(1), 153-163, 2005.

689 Lelieveld, J., Crutzen, P.J., Dentener, F.J., Changing concentration, lifetime and climate forcing of
690 atmospheric methane. Tellus 50B, 128–150, 1993.

691 Lidstrom, M. E., Somers, L.: Seasonal study of methane oxidation in Lake Washington. Appl. Environ.
692 Microbial. 47, 1255-1260, 1984.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


693 Liss, P.S., Merlivat, L.: Air sea gas exchange rates: introduction and synthesis. In: Buat-Menard, P.
694 (Ed.), The Role of Air Sea Exchange in Geochemical Cycling. D. Reidel, Hingham, MA, 113 – 129,
695 1986.

696 Lu, C.Y., Wong, Y.S., Tam, N.F.Y., Ye, Y., Lin, P.: Methane flux and production from sediments of a
697 mangrove wetland on Hainan IslandChina. Mangroves Salt Marshes, vol. 3,no. 1, p. 41-49, 1999.

698 Mayumi, D., Mochimaru, H., Yoshioka, H., Sakata, S., Maeda, H., Miyagawa, Y.: Evidence for
699 syntrophic acetate oxidation coupled to hydrogenotrophic methanogenesis in the high-temperature
700 petroleum reservoir of Yabase oil field (Japan). Environ. Microbiol. 13, 1995–2006, 2011.

701 Mukhopadhyay S.K., Biswas, H., De, T.K., Sen, S., Sen, B.K., Jana, T.K.: Impact of Sundarbans
702 mangrove biosphere on the carbon dioxide and methane mixing ratio at the NE coast of Bay of Bengal,
703 India. Atmospheric Environment 36 (4), 629–638, 2002.

704 Megonigal, J.P., Hines, M.E., Visscher, P.T.: Anaerobic metabolism: linkages to trace gases and aerobic
705 processes. In Biogeochemistry. Ed. W.H. Schlesinger. Elsevier-Pergamon, Oxford, 317– 424, 2004.

706 Middelburg, J.J., Nieuwenhuize, J., Iversen, N., Hoegh, N., DeWilde, H., Helder, W., Seifert, R.,
707 Christof, O.: Methane distribution in European tidal estuaries. Biogeochemistry 59, 95–119, 2002.

708 Panicker A.S., Pandithurai, G., Beig, G., Kim, D., Lee, D.: Aerosol modulation of ultraviolet radiation
709 dose over four metro cities in India. Advances in Meteorology Article ID 202868, 5 pages, 2014.

710 Parsons, T.R., Maita, Y., Lalli, C.M.: A manual of chemical and biological methods for sea water
711 analysis. New York, Pergamon Press, 1992.

712 Purvaja, R., Ramesh R., Frenzel, P.: Plant-mediated methane emission from an Indian mangrove.
713 Global Change Biology, 10, 1–10, 2004.

714 Panganiban, A. T., Patt, Jr., T. E., Hanson. R. S.: Oxidation of methane in the absence of oxygen in the
715 lake water samples. Appl. Environ. Microbiol. 37, 303-309, 1979.

716 Ray, R., Ganguly, D., Chowdhury, C., Dey, M., Das, S., Dutta, M.K., Mandal, S.K., Majumder, N., De,
717 T.K,. Mukhopadhyay, S.K., Jana, T.K.: Carbon sequestration and annual increase of carbon stock in a
718 mangrove forest. Atmospheric Environment, 45, 5016 – 5024, 2011.

719 Reay, W.G., Gallagher, D., Simmons, G.M.: Sediment water column nutrient exchanges in Southern
720 Chesapeake Bay near shore environments. Virginia Water Resources Research Centre, Bulletin- 181b,
721 1995.

722 Rudolf, K.T., Seigo, S.,: Methane and microbes. Nature 440, 878 – 879, 2006.

723 Rudd, J.W., Taylor, C.W.: Methane cycling in aquatic environments. Adv. Aquatic Microbial. 2, 77-
724 150, 1980.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


725 Rudd, J. W., M., Hamilton, R.D.: Factors controlling rates of methane oxidation and the distribution of
726 the methane oxidizers in a small stratified lake. Arch. Hydrobiol. 75, 522- 538, 1975.
727 Rudd, J. W., M., Hamilton, R.D.: Methane cycling in Lake 227 in perspective with some components of
728 carbon and oxygen cycles. Arch. Hydrobiol. Beih. Ergebn. Limnol. 12, 115-122, 1979.

729 Sansone, F.J., Graham, A.W.: Methane along western Mexican mergin. Limnol. Oceanogr. 49(6), 2242
730 – 2255, 2004.

731 Strangmann, A., Bashan, Y., Giani, L.: Methane in pristine and impaired mangrove soils and its
732 possible effect on establishment of mangrove seedlings. Biology and Fertility of Soils, vol. 44, no. 3,
733 511-519, 2008.

734 Sotomayor, D., Corredor, J.E., Morell, M.J.: Methane flux from mangrove sediments along the
735 southwestern coast of Puerto Rico. Estuaries 17 (1B), 140–147, 1994.
736 Smith, S.D., Banke, E.G., 1975. Variation of sea surface drag coefficient with wind speed. Quarterly
737 Journal of Royal Meteorological Society, 101, 665–673.
738 Utsumi, M., Nojiri, Y., Nakamura, T., Nozawa, T., Otsuki, A., Takamura, N., Watamabe, N., Seki, H.:
739 Dynamics of dissolved methane and methane oxidation in a dimictic Lake Nojiri during winter. Limnol.
740 Oceanogr. 43(1), 10-17, 1998a.

741 Utsumi, M., Nojiri, Y., Nakamura, T., Nozawa, T., Otsuki, A., Takamura, N., Watamabe, N., Seki, H.:
742 Oxidation of dissolved methane in eutropic shallow lake: Lake Kasumigaura, Japan. Limnol. Oceanogr.
743 43(3), 471-480, 1998b

744 Upstill-Goddard, R.C., Barnes, J., Frost, T., Punshon, S, Owens, N. J. P.: Methane in the Southern
745 North Sea: low salinity inputs, estuarine removal and atmospheric flux. Glob. Biogeochem. Cycles, 14,
746 1205–1217, 2000.

747 Vaghjiani, G.L., Ravishankara, A.R.: New measurement of the rate coefficient for the reaction of OH
748 with methane. Nature 350, 406 – 409, 1991.

749 Wang, Z.P., Delaune, R.D., Patrick Jr., W.H., Masscheleyn, P.H.: Soil redox and pH effects on methane
750 production in a flooded rice soils. Soil Sci. Society of America Journal 57, 382-385, 1993.

751 Wayne P.: "Chapter 5: The Earth's Troposphere", Chemistry of Atmospheres, An Introduction to the
752 Chemistry of Atmospheres of Earth, the Planets and their Satellites. Oxford Clarendon Press, 209 – 275,
753 1991.

754 Zhang, G., Zhang, J., Lui, S., Ren, J., Xu, J., Zhang, F. : Methane in the Changjiang (Yangtze River)
755 Estuary and its adjacent marine area: riverine input, sediment release and atmospheric fluxes.
756 Biogeochemistry, 91, 71–84, 2008b.

757

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 |

764

765

766

767

768

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 |

771

772

773

774

775

776

777

778

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


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 ($^oC$) | 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 |

781

782

783

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 |

787

788

789

790

791

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




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 |

795
796
797
798

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




799 **Table 7: Seasonal variation of micrometeorological parameters, methane mixing ratio, biosphere**

800 **– 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 | $1.40 \times 10^{11}$ | $1.67 \times 10^{11}$ | $6.05 \times 10^{10}$ |

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

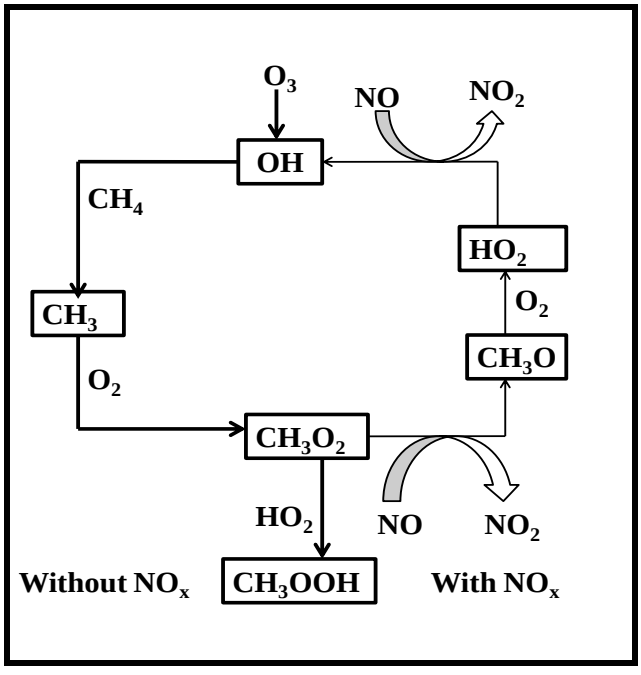




Fig.1: Schematic diagram of atmospheric $CH_4$ photooxidation with/without $NO_x$ concentration.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

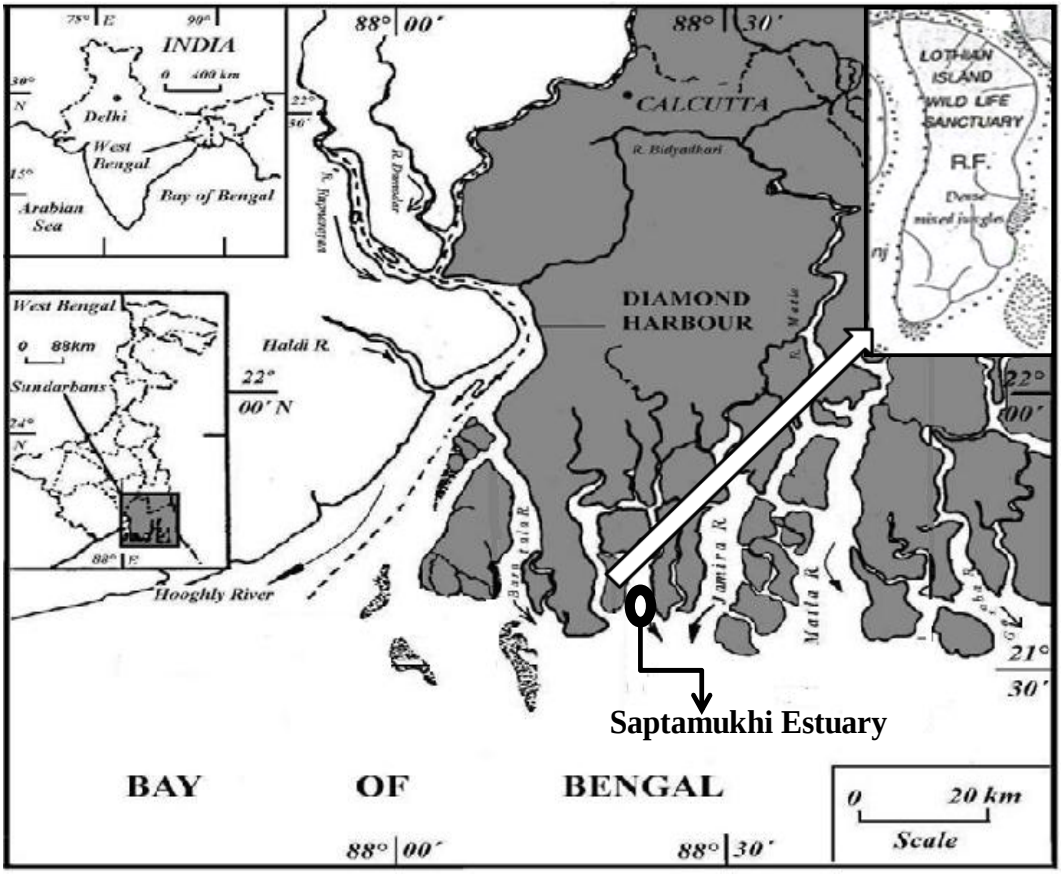
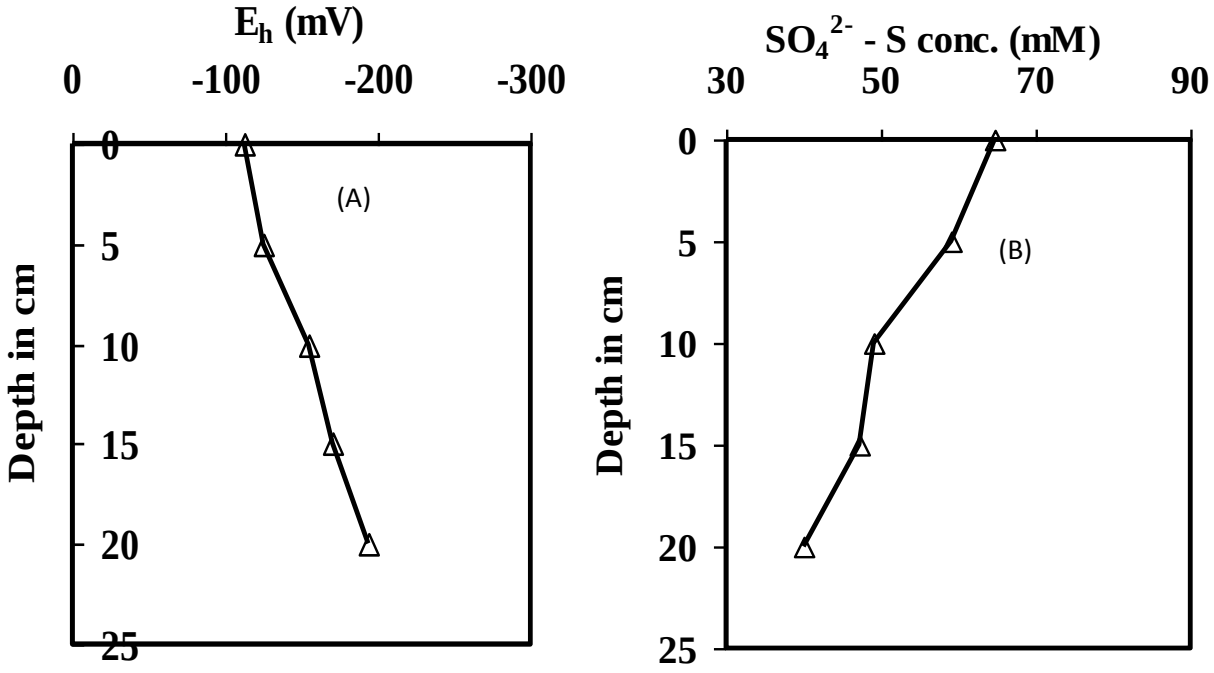



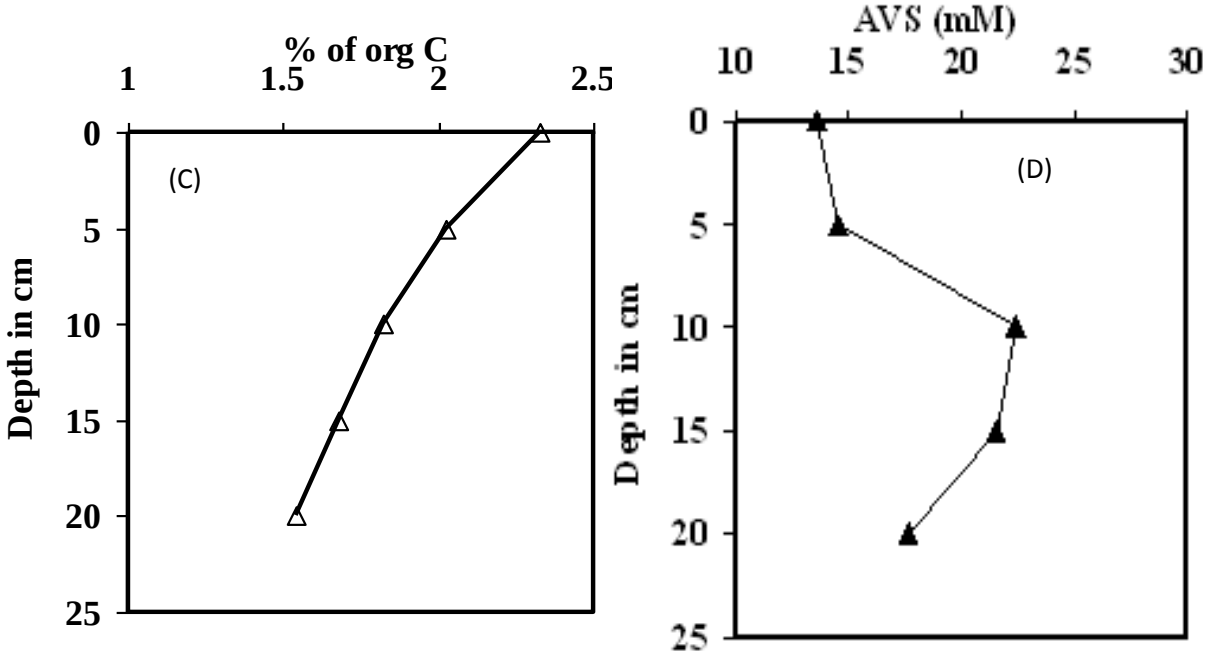

Fig.2: Map showing locations of the study point.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


806

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


807

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

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

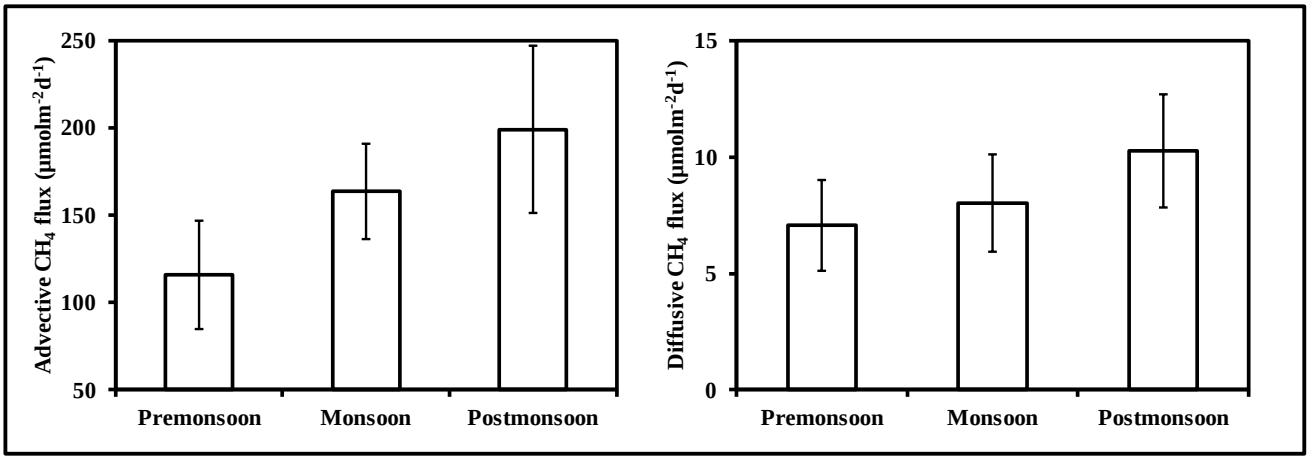




Fig.4: Seasonal variation of advective and diffusive $CH_4$ fluxes from intertidal and subtidal sediments, respectively.

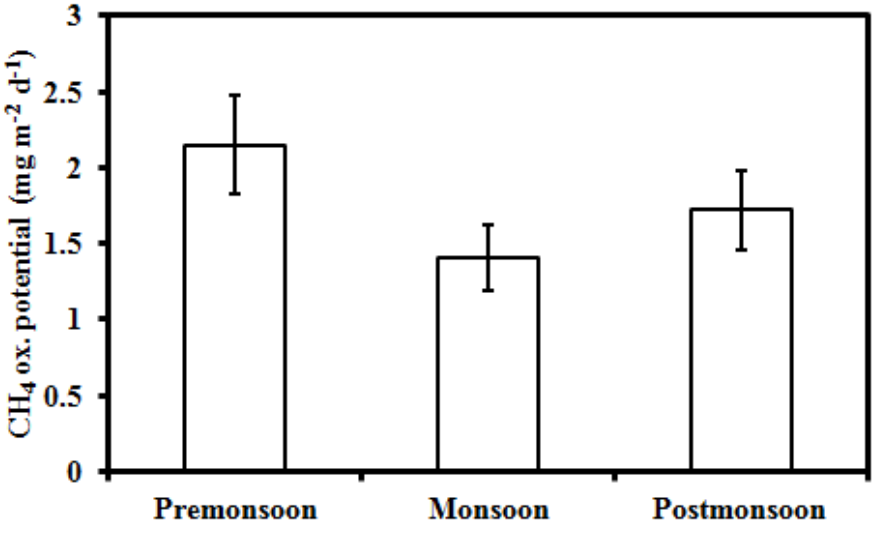
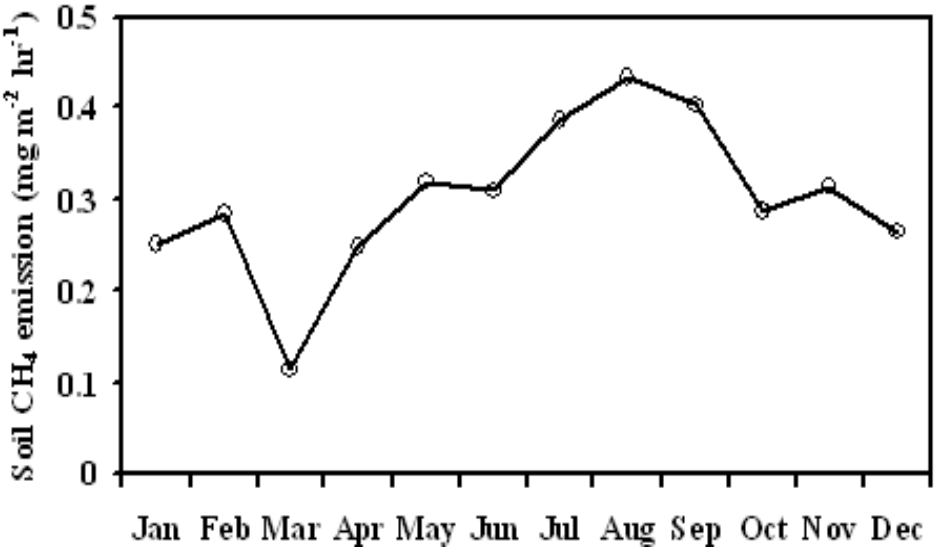


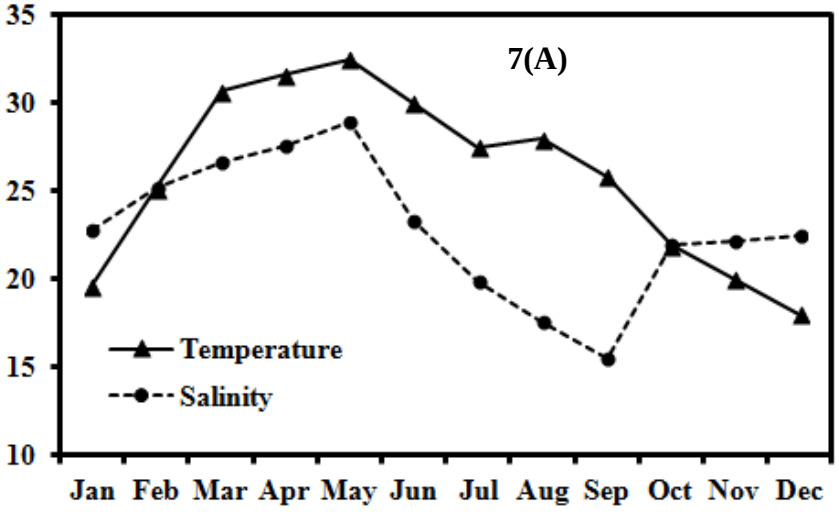

Fig.5: Seasonal variations of surface sediment $CH_4$ oxidation potential in mangrove sediment.

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

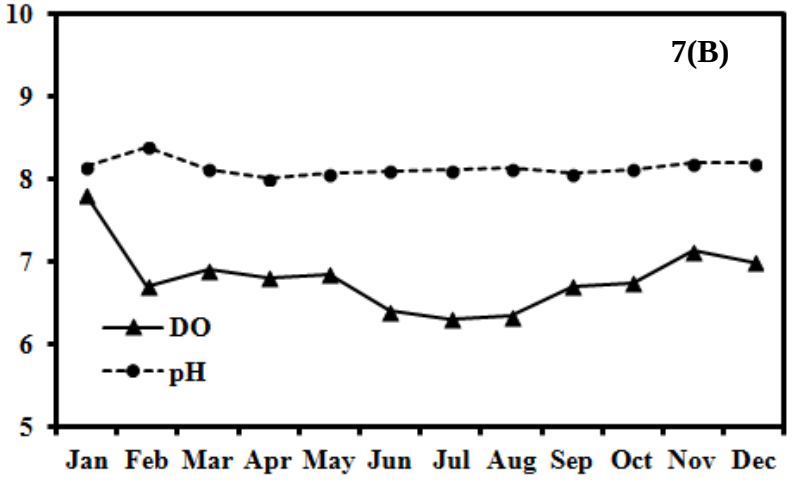

815

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

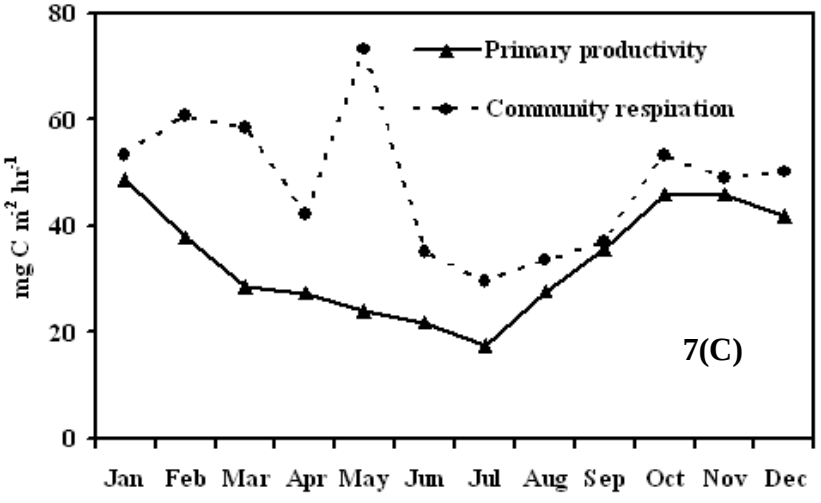



817

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

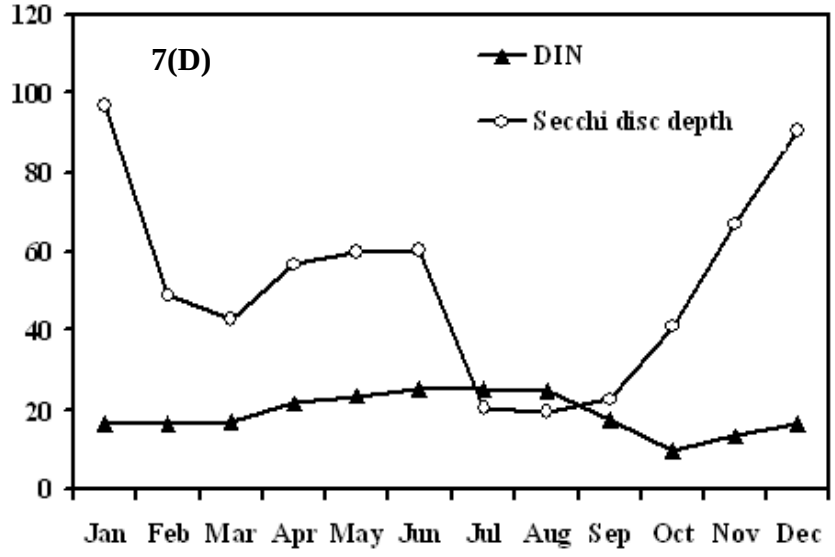




818

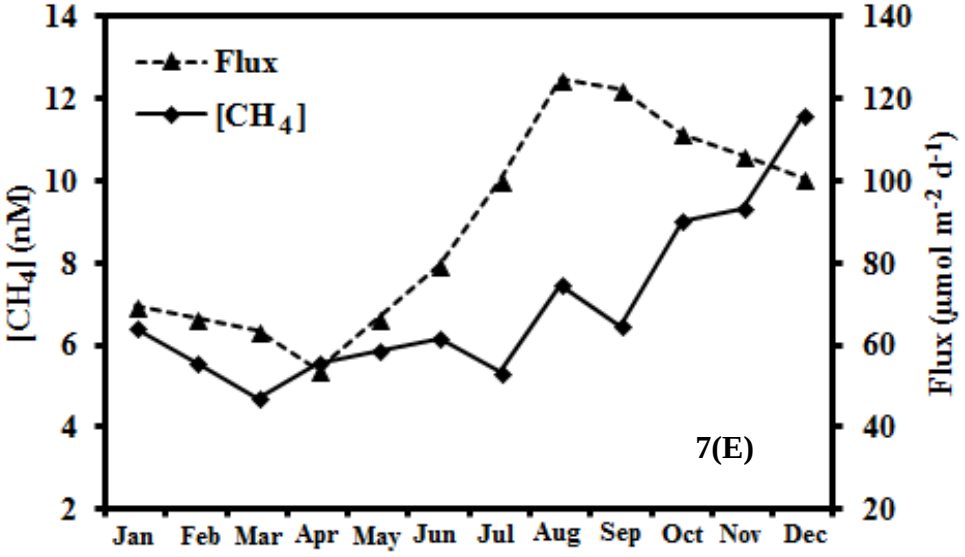


Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016




824

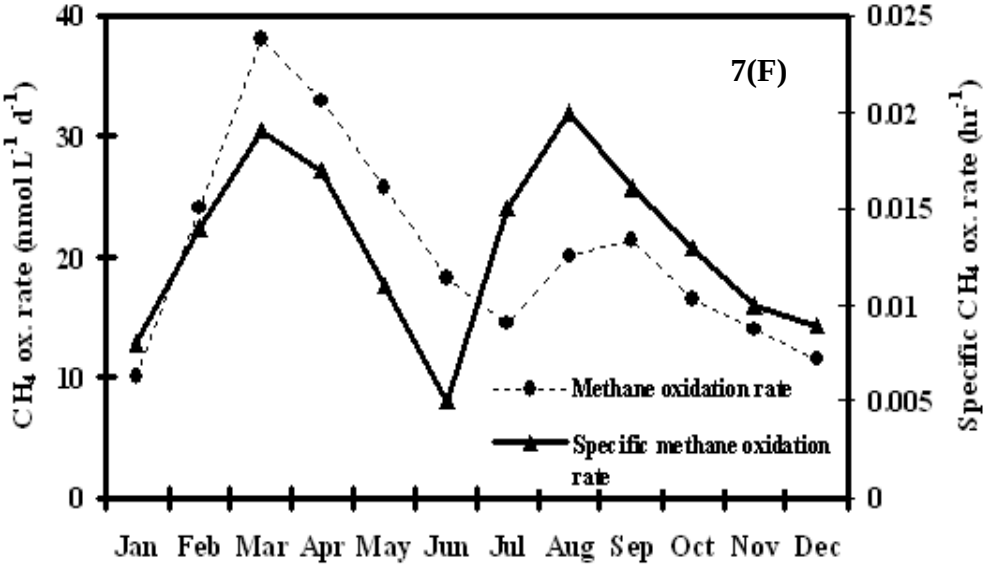



825

826

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

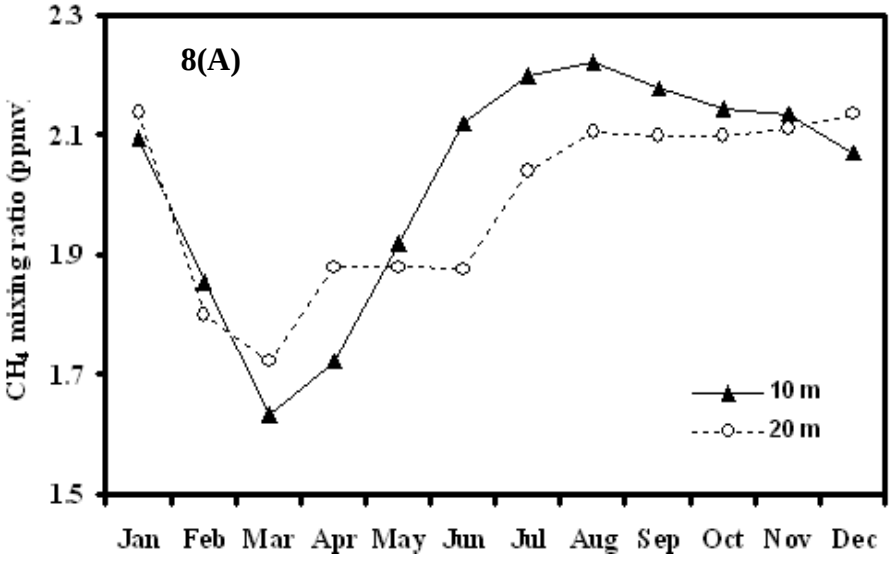



827

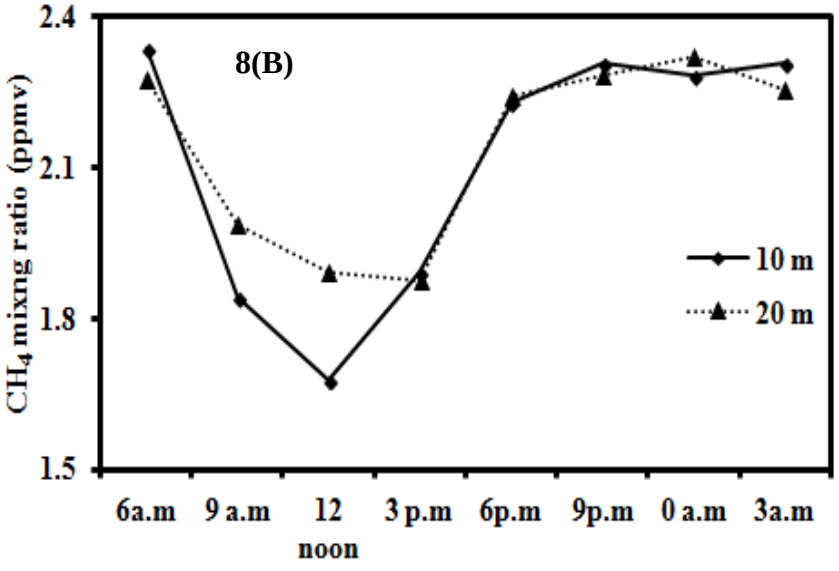
828 Fig.7: Monthly variation of physicochemical parameters along with dissolved methane concentrations,

829 methane oxidation and air-water methane exchange flux.

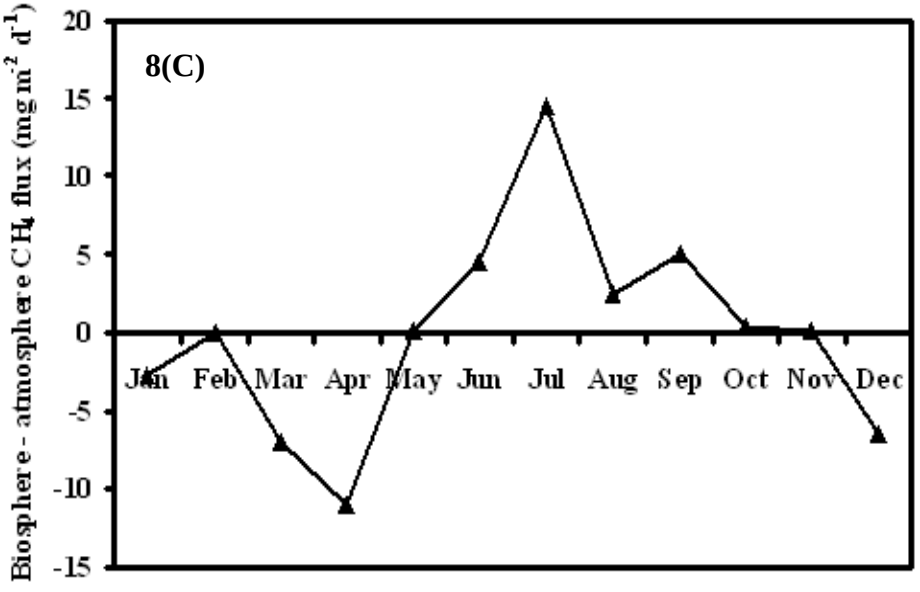



830

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016

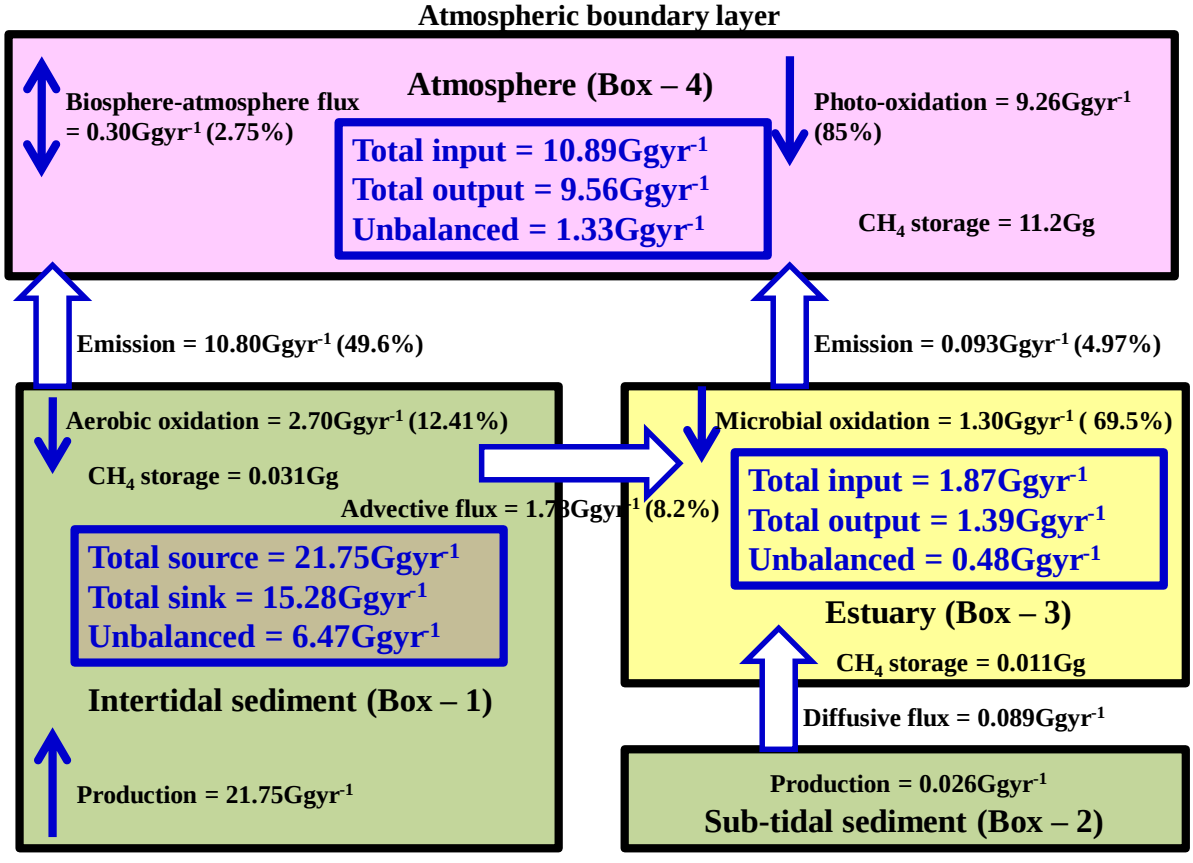

831




832

Biogeosciences Discuss., doi:10.5194/bg-2016-58, 2016
Manuscript under review for journal Biogeosciences
Published: 25 February 2016


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.




836

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

838