CHAPTER 3

MATERIAL AND METHODS

- Sampling of water and air
- Measurement of $\text{CO}_2$ in atmosphere and surface sea water
- Measurement of atmospheric methane
- Measurement of atmospheric $\text{NO}_x$ and $\text{O}_3$
- Measurement of mangrove leaf parameters (protein, LNRA, chlorophyll)
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- Measurement of $\text{H}_2\text{S}$ in air and water
- Determination of water parameters
- Estimation of trace gas fluxes
- Measurement of energy partitioning
- Tidal cycle in the study area and the software used
MATERIAL AND METHODS

3.1 Sampling of water and air

Measurements were carried out in each month during 2006-2008 at station 1 and station 2. With a view to compare the results obtained at station 1 and 2 measurements were also made during three seasons, pre-monsoon (May, 2008), monsoon (September, 2008) and post-monsoon (January, 2009) at station 3 and 4.

Air samples were collected from 10m and 20m at station 1 and station 2 and from 10 and 30 m at station 4 with the help of a portable air sampler (AS2-Technovarian) at a rate of 2.1 min⁻¹ (for CO₂ and CH₄) and drawn into a pre-evacuated glass-sampling bulb of 150 ml capacity fitted with rubber septum. Soon after collection glass sampling bulbs were sealed properly with parafilm and kept in a cool and dry place and transported to the laboratory for the determination of CO₂ and CH₄ by GC (Varian 3800). For diurnal variation, air samples were also collected at every 3 hours interval covering 24 hrs. Meteorological parameters like air temperature, atmospheric moisture content, atmospheric pressure and wind velocity at these stations were recorded simultaneously by using probes and an anemometer connected with computerized weather station (Model No. Davis 7440). Climate sensors were scanned in every 5 min and 1 hr average were recorded. Air for NOx, H₂S and O₃ was scrubbed through impinger with different absorbing mediums for a specific length of time and with a constant flow.

Surface estuarine water was collected at every 6 hrs interval in a tidal cycle for the analyses of different physicochemical parameters. Pore-water and surface sediment samples were collected from several points of the vegetated littoral zone during low tidal exposure.
3.2 Measurement of atmospheric CO₂ at station 1, 2 and 4

Gas chromatographic method

1ml of air sample or standard gas was injected into the injection port with the help of gastight syringe. Carbon dioxide was converted to methane after passing through Methanizer (Model No. MTN-1) maintained at 350°C. Temperature of chrompack capillary column (12.5 m, 0.53 mm) and FID were maintained at 50 and 150°C, respectively. Followed by its determination with FID standard carbon dioxide (320 ppm), procured from EDT Instruments Ltd. was used for calibration. Finally mixing ratio of CO₂ in the air sample was determined by comparison of peak areas for samples and standard. The relative uncertainty on CO₂ measurement was found to be ± 0.063.

3.3 Measurement of CO₂ in surface sea water at station 3

Surface water samples were collected at 3 hrs intervals for 24 hr from an anchored mechanized boat, covering three seasons: pre-monsoon (18th May 2008), monsoon (15th September, 2008), post-monsoon (9th January, 2009). Total alkalinity (TA) was measured by Gran electro titration using 50ml GF/F filtered samples with a reproducibility of ±2 μM kg⁻¹ and estimated accuracy of ±3 μM kg⁻¹. pH was measured using combined electrode (Systronics, μ pH system 362) with a reproducibility of ±0.001 pH units. pCO₂ and DIC were computed from the pH and TA measurements (Frankignoulle and Borges, 2001).

3.4 CH₄ measurement in air at station 1, 2 and 4

1ml of air sample or standard gas was injected into the injection port with the help of gastight syringe followed by its determination with FID to record respective peak area against retention time. Standard methane (2.8 ppmv), procured from EDT Instruments Ltd. was used for calibration. Finally mixing ratio of CH₄ in the air sample was determined by
comparison of peak areas for samples and standard. The relative uncertainty (standard deviation relative to mean value) was found to be and ± 0.09 for CH₄ measurements.

3.5 Measurement of atmospheric NOₓ and Ozone

The sample trend for the measurement NOₓ and ozone in ambient air consisted of the pre-filter and holder, followed by a rotameter, bubbler and air pump (Technovarian AS2).

3.5.1 Estimation of atmospheric NOₓ

Samples were collected from 10m and 20m at station 1 and 2 both sites and air was bubbled through 25 ml of absorbing solution (Sodium hydroxide and Sodium aresenite solution). 25 ml absorbing solution was kept side by side without scrubbing during the sample run for field blanks. After 3 hours run (1 L min⁻¹) contents were quantitatively transferred and mixed with H₂O₂ (0.024%), sulphanilamide and N, (1-Naphthal) ethylene diamine di-hydrochloride (NEDA). After 10 minutes colour development interval NOₓ was estimated by spectrophotometric method with relative error of accuracy ±3.62 % (Jacobs and Hochhieser, 1958; APHA, 1977).

3.5.2 Estimation of atmospheric O₃

15 ml of absorbing solution (0.5% solution of 1, 2-di-(4-pyridyl) ethylene in glacial acetic acid) was used and after scrubbing air for 0.5 h at a rate of 0.5 L min⁻¹, 10 ml of the mixture was allowed to react with 1 ml of 0.2% aqueous solution of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (3-MBTH). After this addition the reaction mixture was then allowed to heat in boiling water bath for 20min for yellow colored azine formation. Then it was cooled under the tap water and absorbance was measured at 442nm against a non-aerated blank prepared from absorbing medium that stood in the laboratory for the same length of time as the absorbing solution used in sampling (Hauser and
Bradley, 1966). Pyridine 4 aldehyde in glacial acetic acid was used as standard to calibrate the method. A precision range of ±1% was obtained.

3.6 Measurement of Mangrove leaf parameters

To examine the soil as one of the sources of nitrogen for protein synthesis by plants leaf protein, total inorganic nitrogen in the soil and leaf nitrate reductase activity were measured.

3.6.1 Total leaf protein

Leaf samples were collected from 10m heights. Total leaf protein was estimated by extracting 500mg of the sample with phosphate buffer. The mixture was centrifuged and the supernatant was used to estimate protein by Lowry’s method (Plummer, 1971).

3.6.2 Leaf nitrate reductase activity

1 g leaf of different mangrove species was homogenized under ice cold condition using 6 ml medium containing 1 mM EDTA, 25 mM Cystine and 25 mM Potassium Phosphate buffer adjusted to a final pH 8.8 with Potassium hydroxide. The extract was centrifuged and 0.2 ml of each extract were used for the change of NADH dependant nitrate reduction to nitrite followed by its subsequent determination by spectrophotometric method using sulphanilamide and naphthyl-ethylene-diamine reagent (Hageman and Reed, 1980).

3.6.3 Leaf chlorophyll

1 gm of finely cutted leaf samples were grind to fine pulp with the addition of 20 ml of 80% acetone in a clean mortar. Mixture was centrifuged for 5 min at 5,000 rpm and the supernatant was transfer into a 100ml volumetric flask. Residue was again grinded with 20 ml of 80 % acetone, centrifuged and supernatant was transferred into the same volumetric flask. This procedure was repeated for several times until the residue became colourless.
Mortar was also washed with 80% acetone and clear washings were transferred into the same volumetric flask. Remaining volume was made up to 100 ml with 80% of acetone. Absorbance was read of the solution at 645, 663 and 652 nm against the solvent (80% acetone) blank. Amount of chlorophyll present in the extract was calculated in mg chlorophyll per g tissue using the following equation:

\[ \text{mg total chlorophyll/g tissue} = 20.2 (A_{645}) + 8.02 (A_{663}) \times \frac{V}{1000 \times W} \]

Where \( A \) = absorbance at specific wavelengths,

\[ V = \text{final volume of chlorophyll extract in 80% acetone}, \]

\[ W = \text{fresh weight of tissue extracted}. \]

Leaf area was measured by plotting 10 matured and fresh leaves of mangrove species over a graph paper. Mean area and leaf weight was used to express total chlorophyll in unit area.

3.7 Determinations of soil parameters

For the determination of total inorganic nitrogen 30 g of soil sub sample collected from the surface (0-10 cm) was immediately extracted in 75 ml of 2 mol L\(^{-1}\) potassium chloride (KCl). The mixture was shaken until well mixed and allowed to stand over night. After 24 hours, 4ml of the supernatant was collected for the estimation of ammonia-nitrogen (NH\(_4^+\)-N), nitrate-nitrogen (NO\(_3^-\)-N) and nitrite-nitrogen (NO\(_2^-\)-N) by spectrophotometric method (Riley and Vitousek, 1995).

3.7.1 Nitrate -Nitrogen

All nitrates present in the sample water were converted to nitrite by reduction. A glass column packed with copper coated cadmium cheeps was used for reduction. Method based on the formation of azo dye. The method for determination of total nitrate and nitrite consists of treating 100 ml of water sample was mixed with ammonium chloride solution.
(2 ml of 25%) and passed through the amalgamated cadmium reduction column with a speed of 2 drops s\(^{-1}\). The eluent (50 ml) collected from the column was then treated with 1 ml solution of sulphanilamide; the resultant diazonium ion was coupled with 1 ml of N-(1-naphthy-ethylene diamine dihydrochloride to give an intensely pink dye. The absorbance of the resulting pink solution was measured photometrically at 543 nm against a reagent blank. Efficiency of the reduction column (>90%) was tested periodically with standards and was subjected to identical treatment in each batch. The concentration of total nitrate and nitrite was computed from calibration curve.

3.7.2 Determination of Ammonia in soil [Phenol – hypochlorite method (Grasshoff, 1983)]

50 ml of suitably diluted soil extracted solution was taken and 2 ml phenol solution (10 gm phenol in 100 ml ethyl alcohol) was added followed by addition of 2 ml nitroprusside solution (0.5 gm sodium nitroprusside per 100 ml deionized water) and 5 ml oxidizing reagent (mixture of 10 gm sodium citrate and 1 gm NaOH in 100 ml deionized water and 25 ml sodium hypochlorite solution, 3.5%). Sample was mixed well by swirling between the additions. The whole mixture was placed in thermostat (maintained at 40 – 45°C) for 30 minutes and was kept in room temperature for more than one hour to develop blue color. A series of working standard solution (1 – 5 \(\mu\)M) was prepared and were treated as the same way of sample for calibration. The method essentially consists of formation of monochloroamine by the reaction of ammonium with hypochlorite, which on reaction with phenol in alkaline medium (pH \(\geq 10\)) in presence of trisodium citrate and nitroprusside (catalyst) gives an intensely colored indophenol blue. Precipitation of Ca and Mg is prevented by the use of citrate as complexing reagent. Ammonia – free de-ionized water
was used throughout the procedure. The absorbance of the resulting blue color was measured at 630 nm against a reagent blank and the concentration of \( \text{NH}_4^+ - N \) was computed from the calibration curve.

### 3.7.3 Determination of Organic Carbon in soil

1 gm of dried soil sample was taken into a 500 ml conical flask. 10 ml of 1N potassium dichromate solution along with 20 ml silver sulphate solution (1.25 gm silver sulphate dissolve in 100 ml concentration sulphuric acid) was added into it and allowed to stand for 30 min for digestion. Mixture was diluted to 200 ml with distilled water. After dilution 10 ml of ortho-phosphoric acid was added into it. Mixture was then titrated against Mohr salt solution (393.13 gm ferrous ammonium sulphate dissolve in 50 ml concentrated sulphuric acid and volume was made up to 1L) in presence of 1 ml diphenyl amine indicator until violet colour of the mixture changed into brilliant green at the end point and following equation was used for organic carbon.

\[
\% \text{ of organic carbon} = \frac{(V_1 - V_2)}{W} \times 0.003 \times 100
\]

Where 

\(V_1\) = Volume of Mohr salt required to titrate 

\(V_2\) = Volume of Mohr salt required to titrate 10 ml potassium di-chromate as blank

\(W\) = Weight of the sediment sample taken

\% of organic matter = \% of organic carbon \times 1.724

### 3.8.1 Measurement of \( \text{H}_2\text{S} \) in air

Atmospheric \( \text{H}_2\text{S} \) concentrations were estimated at 1 and 10 m above the ground and their difference was used to calculate soil emission (Barrett, 1998). \( \text{H}_2\text{S} \) in air was estimated by drawing air samples with the help of a portable air sampler (Technovarian air sampler model AS2) through 25 ml absorbing solution (alkaline \( \text{CdSO}_4 \)) placed in bubbler for
samples. A separate set was also run side by side for field blanks. Finally H₂S was determined using standard methylene blue method (Moest, 1975; Lodge and James, 1989). Exchange flux of H₂S between the biosphere and the atmosphere, F, was calculated using the relation (Barrett, 1998):

3.8.2 Measurement of dissolved H₂S in water

The H₂S concentration of pore water and surface water samples were determined according to the colorimetric methylene blue method described by Fonselius (1983). In this method a 1:1 mix of N, N-dimethyl-p-phenylene diamine dihydrochloride and ferric chloride solution was used. The absorbance of the mixture was measured at 670 nm.

3.9 Determination of water parameter (APHA, 1995; Grasshoff et al., 1983)

3.9.1 Sulphate

Turbidimetric method was used to measure dissolved sulphate in pore water and surface water. The method involves an addition of barium chloride and a conditioning reagent consisting glycerol, ethanol and HCl. The sulphate combines with Ba²⁺ to precipitate as BaSO₄. The turbidity of the sample was then measured at 420 nm.

3.9.2 Determination of salinity

Chlorinity (Cl) of both surface and pore water were determined by Mohr-Knudsen titration method and standard seawater of chlorinity 19.374 procured from the National Institute of Oceanography Goa, was used for the standardization. 15 ml of sample water with the help of a cleaned and dry pipette and 25 ml of chloride free distilled water was mixed with the sample. 6 drops of 8% potassium chromate solution was added as indicator. Whole mixture was titrated using silver nitrate solution (36.75 g L⁻¹). At the end point colour of the mixture was changed.
to red. Standard seawater of chlorinity $19.374 \times 10^{-3}$ was also titrated following the same procedure.

From the knowledge of chlorinity, salinity ($S$) was calculated using the Knudsen relation: $S \left( \times 10^{-3} \right) = 1.80655 \times \text{Cl} \left( \times 10^{-3} \right)$

### 3.9.3 pH

Seawater pH was determined by using micro pH meter (Systronics, model No, 362).

### 3.9.4 Dissolved iron

Dissolved iron in filtered (0.45 μm) surface and pore water were estimated by standard spectrophotometric method. Iron [Fe (II)] forms a violet colour complex when treated with 2, 4, 6-tripyridyl, 1, 3, 5-triazine (TPTZ) in weak acid solution ($pH = 3.5$ to 5.8). Ascorbic acid was used to reduce Fe (III) to Fe (II). The absorbance of the violet colour was measured at 595 nm.

### 3.10 Estimation of Fluxes

#### 3.10.1 Biosphere-atmosphere exchange

Micrometeorological method was applied for trace gas exchange over Sundarban biosphere due to its source uniformity with large area (9630 km$^2$) (Phillips et al., 2004; Flesch et al., 2002; Oke, 1978). Parrish et al. (1987) extensively intercompared the gradient method with enclosure technique and excellent agreement between these two independent methods was obtained over a three-order magnitude range of soil NO$_x$ emission.

#### 3.10.1. a Calculations for the measurement of trace gases fluxes

The rate of exchange of trace gases between biosphere and atmosphere was calculated considering aerodynamic ($r_a$), surface layer ($r_s$) resistance, canopy resistance ($r_c$) and the concentration difference, $\Delta z = z_{10} - z_{20}$ for forest cover area at two heights $z_1$ and $z_2 (z_2 > z_1)$. 

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Exchange velocity, $V_c$ defined as $1 / (r_a + r_s + r_c)$ and net flux, $F$ was calculated using the relation (Barrett, 1998):

$$ F = V_c \times \Delta^2 $$

Negative $F$ indicates net transfer from the atmosphere to the biosphere and positive $F$, for emission. The confidence limit of the flux measurement is calculated by:

$$ \bar{x} \pm ts/\sqrt{N} $$

where $\bar{x}$ is the mean values, $s$ is the standard deviation, $N$ is the number of observations, $t$ is the statistical factor that depends on the number of degree of freedom and the confidence level derived (Christian, 2001). $r_a$ can be defined as the resistance for transfer of a particular trace gas along with heat energy from a horizontally homogeneous vegetated surface to a reference level, $z$, above the canopy in adiabatic conditions and it was evaluated from the relation (Wesely and Hicks, 1977):

$$ r_a = \frac{\ln (Z/Z_0) - \Psi_c}{k u^*} $$

Where $Z_0$ is roughness height and $\Psi_c$ is a correction function for atmospheric stability. It serves to increase $r_a$ for stable condition and decrease it for unstable condition. The equations for the correction functions are (Wesely and Hicks, 1977):

$$ \Psi_c = -5 \frac{Z}{L} \text{ for } 0 < Z/L < 1 \text{ (Stable condition) and } $$

$$ \Psi_c = \exp [0.0598 + 0.39\ln (-Z/L) - 0.09 (\ln (-Z/L))^2] $$

for $0 > Z/L > -1 \text{ (Unstable condition) }$

The correction functions are expressed in terms of a stability parameter $Z/L$ (Obukhov, 1971), in which $Z$ is the height and $L$ is the Obukhov Scale length. From the wind speed values $u_2$ and $u_1$ at two heights $Z_2$ and $Z_1$, the friction velocity, $u^*$ was calculated as:
\[ u^* = k \left( \frac{u_1 - u_2}{\ln(Z_2/ Z_1)} \right), \]

where k is the Von Karman constant. \( Z_0 \) was determined by plotting the wind profile as \( \ln Z \) versus \( u \). The slope of the resulting straight line is \( k/u^* \) and the intercept is \( \ln Z_0 \). For forest cover a displacement length, \( d \) equal to 80% of the average height of the roughness element (mangrove plants: average height 10m) was considered (Panofsky and Dutton, 1984). The scale length, \( L \) was evaluated using of stability classes such as these of Pasquill range from A - F (Pruppacher and Klett, 1978). A relation between the Pasquill stability classes, the roughness length \( Z_0 \), and \( L \) as given by Golder (1972) was used for calculation of \( 1/L \):

\[ 1/L = a + b \log Z_0 \]

Where 'a' ranges between 0.035 and - 0.096 and 'b' ranges between 0.029 and -0.036.

Surface layer resistance (\( r_s \)), for forest cover was calculated using the following relation (Wesely and Hicks, 1977):

\[ k B^{-1} = 2(K/Dc)^{2/3} \]

and \( r_s = B^{-1}/u^* \)

where \( B^{-1} \) is transfer function, k is the Von Karman constant, K is the thermal diffusivity of air and \( Dc \) is the molecular diffusivity: \( Dc = D_0 \left( \frac{T_2}{273} \right)^{1.5} \), where \( T_2 \) is the temperature at 20 m height and \( D_0 \) (\( \text{cm}^2 \text{s}^{-1} \)) is 0.115 for NOx and 0.124 for \( O_3 \). \( Dc \) values are 0.22 and 0.155 for \( CH_4 \) and \( CO_2 \), respectively at 25°C. For canopy resistance (\( r_c \)) following relation was used (except \( H_2O \) vapour):

\[ r_c = \left[ \ln (z-d) - \psi_c / ku^* \right] - (r_a + r_s), \]

Where \( d \) is zero plane displacement, being in the range 0.7 to 0.8 of mean plant height (h) (Panofsky and Dutton, 1984; Hicks, 1989).
3.10.1.b Storage error for CO\textsubscript{2} and CH\textsubscript{4}

The planetary boundary layer (PBL) height (h) was estimated (Pal Arya, 2001) using the relation: \( h = 0.25 \frac{u^*}{|F|} \) and \( u^* \) (frictional velocity) was calculated from wind velocity (u) at two different heights, \( z_1 \) and \( z_2 \) using relation \( u^* = k \left( \frac{u_{z_2} - u_{z_1}}{\ln \left( \frac{z_2}{z_1} \right)} \right) \), where \( k \) is Von Karman constant (0.4) and \( F \) is Coriolis parameter related to the rotational speed of the Earth (\( \Omega \)) and latitude \( \varphi \) as \( F = 2 \Omega \sin \varphi \).

Storage rate from sea source during stable condition and land advection from anthropogenic source (x) for concentration (C) in the surface layer between \( z_1 \) and \( z_2 \) m height were calculated using the relations (Fowler and Duyzer, 1989):

\[
\Delta \text{(storage)} = \frac{\partial C}{\partial t} (z_2 - z_1) \quad \text{and} \quad \Delta \text{CO}_2 \text{ (advection)} = u \cdot \frac{\partial C}{\partial x} (z_2 - z_1)
\]

Mean storage error (at station 1 and 2) for methane was found to be \( \leq 0.01\% \) and Advection errors at 10 m height varied between 0.001 and 4.15%.

3.10.2 Water-air exchange

The air-water CO\textsubscript{2} flux (\( \mu \text{Mm}^{-2}\text{h}^{-1} \)) was computed according to: \( F_{\text{CO}_2} = \alpha k \Delta p_{\text{CO}_2} \), where \( F_{\text{CO}_2} \) is the air-water CO\textsubscript{2} flux, \( \alpha \) is the CO\textsubscript{2} solubility coefficient (\( \text{mM m}^{-3} \text{ppm}^{-1} \)), \( k \) is the gas transfer velocity (\( \text{m d}^{-1} \)) and \( \Delta p_{\text{CO}_2} \) is air-water gradient of CO\textsubscript{2} (\( p_{\text{CO}_2\text{water}} - p_{\text{CO}_2\text{air}} \) (10m) in ppm), \( k \) was computed according to a parameterization as a function of wind speed, water current and depth (Borges et al., 2004),

\[
k_{600} = 0.24 + 0.4126 w^{0.5} h^{-0.5} + 0.619 u_{10},
\]

where \( k_{600} \) is the gas transfer velocity of CO\textsubscript{2} normalized to a Schmidt number (\( S_c \)) of 600 in m d\textsuperscript{-1}, \( w \) is the water current (cm s\textsuperscript{-1}), \( h \) is the water depth (25 m) and \( u_{10} \) is the wind speed (m s\textsuperscript{-1}) referenced at a height of 10m.

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3.11 Measurement of water vapour and related parameters

The partial pressure of water vapour was calculated from the relation:

$$P_{H_2O} = \frac{h}{100}P_0,$$

where $h$ is relative humidity and $P_0$ is the vapour pressure at a given temperature:

$$\ln P_0 = -0.493048 + 0.07263769t - 0.000294549t^2 + 9.79832 \times 10^{-7}t^3 - 1.86536 \times 10^{-9}t.$$

Following equation was used to calculate the rate of evapotranspiration or water vapour flux (mg m$^{-2}$ s$^{-1}$):

$$ET \text{ or } E = \left[\frac{\rho_t}{(1.6 \times p)}\right] \times \left[\frac{(P_{H_2O(10 \text{ m})} - P_{H_2O(20 \text{ m})})}{(ra + r_s + r_c)}\right]$$

Where, $\rho_t$ is density of air, $p$ is atmospheric pressure. In order to express Evapotranspiration in terms of MJ m$^{-2}$ s$^{-1}$, ET (mg m$^{-2}$ s$^{-1}$) was multiplied by $\lambda$, where $\lambda =$ Latent heat of Vaporization = 2.45 MJ Kg$^{-1}$.

Latent heat flux (w m$^{-2}$), $H_l = ET \times \lambda$, can also be derived from the same equation.

Canopy resistance ($r_c$) (in s cm$^{-1}$) for the water vapour by the tropical mangrove ecosystem was calculated using the following equation obtained by Monteith model (Tan and Black, 1976):

$$r_c = \left[\rho_t c_p (e_s - e_d)/(\gamma ET)\right] + ra \left[\frac{\Delta \gamma(A/ET - 1)}{\gamma(A/ET - 1)} - 1\right]$$

where $A =$ available energy for evapotranspiration: ($R_n - H_G - H_s$) (W m$^{-2}$)

$c_p =$ specific heat of moist air (J kg$^{-1}$ K$^{-1}$)

e$_s =$ saturation water vapour pressure at height $d$ (mb)

e$_d =$ water vapour pressure at height $d$ (mb)

$r_s =$ aerodynamic resistance (s cm$^{-1}$)

$R_N =$ net solar radiation (W m$^{-2}$)

$H_G =$ ground heat flux (W m$^{-2}$)
$H_s =$ storage heat energy ($W \ m^{-2}$)

$\Delta =$ slope of the saturation water vapour pressure curve ($mb \ K^{-1}$)

$\gamma =$ psychrometric constant ($mb \ K^{-1}$)

Equilibrium evapotranspiration ($ET_{eq}$) is defined as evaporation from a wet surface into saturated air (Priestley, 1959). Equilibrium evaporation occurs when air passes over an extensive wet surface and becomes saturated. Then, the Bowen ratio ($\beta = H/LE$ where $H$ and $LE$ are the sensible and latent heat flux, respectively) takes the value $\gamma/\Delta$, where $\Delta$ is the changing rate of saturation water vapor pressure with temperature ($Pa \ K^{-1}$), and $\gamma$ is the psychrometric constant (66.5 $Pa \ K^{-1}$). Under this condition, the daily equilibrium evaporation ($ET_{eq}, MJ \ m^{-2} \ d^{-1}$) was obtained using the energy balance equation as follows (Priestley and Taylor, 1972):

$$ET_{eq} = \Delta (R_n - G) / (\Delta + \gamma)$$

Where, $R_n$ is the daily net radiation above the canopy ($MJm^{-2} \ d^{-1}$). $G$ is the ground heat flux ($MJ \ m^{-2} \ d^{-1}$). The thermodynamic variable $\Delta$ was calculated based on the mean air temperature averaged over daylight hours. Daily net radiation was obtained by averaging these hourly values.

The slope of the saturation vapour pressure curve is calculated as (Allen et al., 1998):

$$\Delta = 4098 \ [0.6108 \ exp(17.27 \ T_{mean}/(T_{mean} + 237.3))] / (T_{mean} + 237.3)^2$$

where: $\Delta =$ slope of the saturation vapour pressure curve ($kPa \ °C^{-1}$) at $T_{mean}$.

$T_{mean} =$ daily mean air temperature at 2 m height [°C].
Total evapotranspiration was considered as mainly transpiration with small error for forests with no intercepted water present, since evaporation from the soil is small. According to the Penman-Monteith model of transpiration assumes that the canopy is isothermal and that the canopy resistance \( r_c \), is the resistance of all stomata of the leaves acting in parallel, depends primarily on solar radiation, vapour concentration deficit and soil moisture deficit.

Saturation vapor pressure, \( e_s \) in kPa if temperature, \( T \), is in degrees Celsius (Ward et al., 2004):

\[
e_s = \exp \left( \frac{(16.78 T - 116.9)}{(T + 237.3)} \right)
\]

The equation is valid for temperatures ranging from 0 to 50°C.

**Actual Vapor Pressure (\( e_d \))**

The following equation can be used to find actual vapor pressure (\( e_d \)):

\[
e_d = e_s \times \text{RH}/100
\]

Where, \( e_s \) is the saturation vapor pressure

\( \text{RH} = \) relative humidity in percent

**Vapor Pressure Deficit**

Vapour Pressure Deficit, or VPD, is the difference between the saturation water vapor pressure and the actual water vapor pressure \( (e_s - e_d) \) (Ward et al., 2004) at a particular temperature.

Decoupling coefficient \( (\Omega) \) was calculated using the following equation,

\[
\Omega = \left( \frac{\varepsilon + 1}{\varepsilon + 1 + \left( \frac{r_s}{r_a} \right)} \right)
\]

where \( \gamma \) is the psychometric constant, \( \varepsilon \) is \( \Delta/\gamma \), \( \Delta \) is the slope of the saturation vapour pressure curve, \( r_s \) is the surface resistance, \( r_a \) is the aerodynamic resistance.
3.12 Measurement of energy partitioning

The supply of radiative energy to the Earth and its partitioning maintain a thermal equilibrium at the surface and the surface energy budget is:

\[ R_s \uparrow + R_l \downarrow = H + H_l + H_g + ΔS + (R_s \uparrow + R_l \uparrow), \]

Where, \( R_s \downarrow, R_l \downarrow \) and \( R_s \uparrow, R_l \uparrow \) (\( R_n = R_s \downarrow + R_l \downarrow + R_s \uparrow + R_l \uparrow \)) are the components of incoming and upward short wave and long wave radiation (Wm\(^{-2}\)) respectively. \( H, H_l \) and \( H_g \) are the sensible, latent and ground heat fluxes (Wm\(^{-2}\)) that redistribute the major portion of the insolation; and \( ΔS \) is the energy storage by the system which includes physical, \( ΔH_s (P) \) and the energy consumed by photosynthesis, \( ΔH_s (C) \). The two components of long wave radiation (atmospheric window for 8–14 mm wavelength band) are usually of the same order of magnitude (emissivity, \( ε=1 \) for forest) and depend on surface temperature:

\[ (T_s): R_l \uparrow \text{ or } R_l \downarrow = εσT_s^4, \]

where \( s \) is the Stefan–Boltzmann constant. Contribution of the long wave radiation towards energy budget under clear skies condition is considerably low compared to the short wave radiation (Pal Arya, 2001).

Following equations were used to calculate the sensible heat flux:

\[ H = ρ_t c_p (T_{10m} - T_{20m})/(r_a + r_s), \]

Where, \( ρ_t \) and \( c_p \) are density and specific heat of air respectively.

The storage energy, \( ΔH_s (P) \) was calculated from the change of heat through the forest profile in the air column:

\[ ΔH_s (P) = ρ_t c_p Z (dt/dz)_m, \]
where \((dt/dz)_m\) is the mean (layer averaged) rate of warming of the canopy layer, \(Z\). Energy consumed by photosynthesis, \(\Delta H_\text{S(C)}\) was calculated from the downward flux of \(\text{CO}_2\) (\(\text{mg m}^{-2} \text{ s}^{-1}\)) by day and expressed in \(\text{W m}^{-2}\), considering 1 mole \(\text{CO}_2\) was photosynthetically fixed into 1 mole carbohydrate (~4.1 cal mg\(^{-1}\)).

To measure ground heat flux, \(H_G\) two equations were considered:

\[
(1) \quad H_G = -C_d c_p \rho u_{10} \Delta \theta,
\]

where \(\Delta \theta\) is the difference of air and surface tidal water temperature, \(c_p\) is specific heat of dry air, \(\rho\) is air density and \(C_d\) is friction coefficient (for high tide condition when most of the study area was inundated by tidal water) and

\[
(2) \quad H_G = -k (\delta T/\delta z),
\]

where \(k\) is thermal conductivity of clay/peat soil and \(\delta T/\delta z\) is downward (\(z\) direction) temperature gradient (for low tide condition when mangrove bed was exposed).

Incoming net short wave radiations \((0 < \text{R}_\text{N} \leq 4 \mu\text{m})\) at 1-h interval were obtained by using the Hybrid Single-Particle Langrangian Integral Trajectories (HY-SPLIT) model, National Oceanic and Atmospheric Administration (NOAA) ARL database (NOAA, ARL, website, http://www.arl.noaa.gov/ready.html). SBDART model (version 2.4, August, 2004, Santa Barbara site, University of California) for surface albedo with vegetation at the land–ocean boundary was also used to compute net short wave radiation corrected for aerosol and trace gases (\(\text{CO}_2\), \(\text{CH}_4\), \(\text{N}_2\text{O}\)) at 1 hr interval.

### 3.13 Tidal cycle in the study area

Data regarding daily tidal amplitude was collected website tide table published by Kolkata port trust for Sagar Island, West Bengal. Also tide predictions data collected from [http://www.sailwx.info/index.html](http://www.sailwx.info/index.html) website (heavily modified version of David Flater's...
program Xtide) were used for comparison by a heavily modified version of David Flater's program Xtide. Tidal data for station 3 and 4 were collected from the tide chart published by Paradeep port trust.

3.14 Software used

Microsoft word and Excel were used for data processing. Adobe Photoshop, Microsoft Office paint was used to edit and prepare different Figures. The different sample data were used for different statistical analysis (e.g. stepwise regression analysis, Factor analysis, 't' test, etc.), which was performed using the MINITAB (Version 13.0) and SPSS (10.0) statistical package.