Atmospheric Ozone And Its Biosphere - Atmosphere Exchange In A Mangrove Forest Ecosystem: A Case Study From Sundarbans, NE Coast Of India

Manab Kumar Dutta, Rishmita Mukherjee, Dr. Sandip Kumar Mukhopadhyay

ABSTRACT: Temporal variation of atmospheric O_3 and its biosphere – atmosphere exchange were monitored in the Sundarbans mangrove forest from January 2011 to December 2011 on bimonthly basis. O_3 mixing ratios at 10 m and 20 m heights over the forest atmosphere ranged between 14.66 ± 1.88 to 37.90 ± 0.91 and 19.32 ± 6.27 to 39.80 ± 10.13 ppbv, respectively; having maximal premonsoon and minimal monsoon periods. Average daytime O_3 mixing ratio was 1.69 times higher than nighttime; indicates significant photo chemical production of O_3 in forest atmosphere. Annual averaged O_3 mixing ratio in 10 m height was 13.2 % lower than 20 m height; induces exchange of O_3 across mangrove biosphere – atmosphere interface depending upon micrometeorological conditions of the forest ecosystem. Annual average biosphere – atmosphere O_3 exchange flux in this mangrove forest environment was – 0.441 μg m^{-2} s^{-1}. Extrapolating the value for entire forest surface area, the mangrove ecosystem acts as a sink of 58.4GgO_3 annually, indicating significant contribution of Sundarbans mangroves towards regional atmospheric O_3 budget as well as climate change.

KEYWORDS: atmosphere, exchange flux, India, mangrove, micrometeorology, ozone, Sundarbans.

1. Introduction:

After CO_2 and CH_4, ozone (O_3) is the third most important greenhouse gas in the earth's atmosphere, having a radiative forcing of + 0.35 Wm^{-2} (IPCC, 2001). Each additional molecule of O_3 produced in the atmosphere is 1200 - 2000 times more effective in global warming than an additional CO_2 molecule (Lal et al., 2007). Moreover, oxidizing capacity of the atmosphere is highly influenced by tropospheric O_3 level both through its direct role and through its role as a precursor of the OH radical, which act as initiator of most atmospheric photochemical transformations (Chand and Lal, 2004; Reddy et al., 2008b). Being a potent green house gas and significantly correlated to atmospheric photochemistry, it is a subject of great interest to study atmospheric O_3 which at certain ambient levels may cause damages to vegetation as well as human beings (Finlayson-Pitts and Pitts, 1997; Hogsett et al., 1997). In the forest environment, O_3 is not directly emitted into the atmosphere and it is produced through a complex set of photochemical transformation processes involving NO_x (NO + NO_2) and volatile organic compounds (VOCs) (Fishman and Crutzen, 1978).

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In particular, formation of O_3 in the atmosphere critically depends on ambient NO levels when NO concentrations reach to its critical limit (10 pptv) (Lin et al., 1988). Additionally, the formation of HO_2 and RO_2 in the atmosphere through coupled interactions between CO, NO_x and VOC with OH radical also promote O_3 production in the forest atmosphere (Sillman, 1999). Along with the photochemical O_3 production occurring in the mangrove atmosphere, micrometeorological variables especially sunlight, cloud cover and water vapor concentration play a decisive role in production and distribution of O_3 in the atmosphere. Decreasing sunlight restrains the production of free radicals in the forest atmosphere inhibiting atmospheric photochemical O_3 production (Sillman, 1999). In addition, dry deposition of O_3 on vegetation, water and stratospheric - tropospheric O_3 exchange also contribute partially to regional atmospheric O_3 budget. Dynamics of atmospheric O_3 and its controlling factors have been previously reported by several researchers but till now there is a scarcity of published report on forest ecosystem, especially no reports are available on mangrove forest ecosystem. The primary objective of this paper is to report atmospheric O_3 level and its biosphere – atmosphere exchange in a tropical mangrove forest environment, the Sundarbans. Beyond this primary objective another objective was to study micrometeorological influence on atmospheric O_3 distribution and its biosphere – atmosphere exchange flux.

2. Study area:

Sundarbans (21°32' and 22°40'N : 88°05' and 89°E) is the largest mangrove forest in the world situated at the land ocean boundary of Ganges-Brahmaputra delta and the Bay of Bengal having an area of 10,200 sq km of which, 41% Reserved Forest is spread over India and the rest is in Bangladesh. The Indian part of Sundarbans is extended over an area of 9600 sq km which is demarcated as Sundarbans Biosphere Reserve constituting of 4200 sq km. mangrove reserve forest, 1800 sq. km estuarine waterways and 3600 sq. km. reclaimed areas. The Indian part of the Sundarbans (Fig.1) is crisscrossed by the estuarine phases

of several rivers namely Mooriganga, Saptamukhi, Thakuran, Matla, Bidya, Gosaba and Haribhanga forming a large number of discrete islands. One of these Islands is the Lothian Island, covering an area of 38 km^2 has been notified as a sanctuary and is situated at the confluence of Saptamukhi river and Bay of Bengal. Mangrove like *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. Mangrove plants rarely exceed 10 m in height, and the over-forest trajectory of the wind (fetch) is about 15 km. The Sundarbans has a typical tropical climate having three seasons with four months duration for each season as follows; premonsoon (February - May), monsoon (June - September) and postmonsoon (October - January). The present study has been carried out in the Lothian Island, which can be ideally taken as a representative of Sundarbans mangroves to study atmospheric O_3 and its biosphere – atmosphere exchange flux.

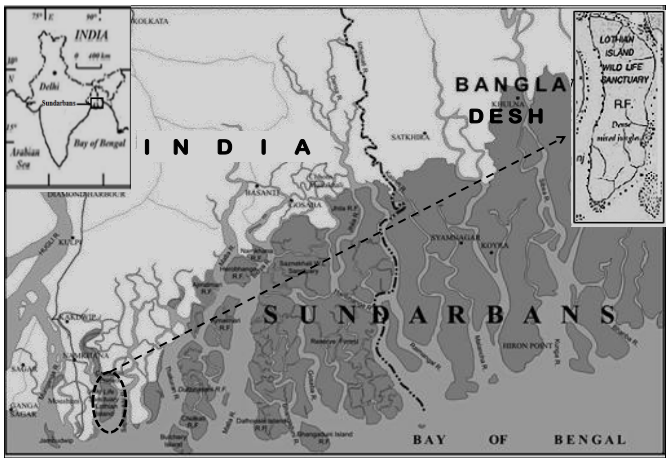

Fig.1: *Map Showing location of the study point.*

3. Materials and methods:

The present study was carried out from January 2011 to December 2011 on bimonthly basis covering diurnal variation in every 3 hours. The atmospheric O_3 samples along with micrometeorological data were collected from 10 m and 20 m height of a watch tower located in the middle of the Lothian Island (21° 42′ N and 88°18′ E).

3.1 Analytical method for estimation of atmospheric O_3 mixing ratio:

Air samples were drawn through 15 ml of absorbing solution (0.5% solution of 1, 2 – di - (4 - pyridyl) ethylene in glacial acetic acid) for 0.5 h at 0.5 $Lmin^{-1}$. Absorbed solution were properly sealed and stored in ice box during transportation to the laboratory. In the laboratory to 10 ml of the solution, 1 ml of the color-developing reagent (0.2 % aqueous solution of 3-methyl-2-benzothiazolinone hydrazone hydrochloride) was added and heated in a boiling water bath for 20 min followed by cooling at room temperature led to formation of yellow-colored azine complex. Standard solutions of concentrations ranging between 0.0 and 10.0 µg of pyridine – 4 - aldehyde per milliliter in glacial acetic acid were used for calibration. Non-aerated blanks were prepared from absorbing solution that stood in the field for the same length of time as the absorbing solution used in sampling. Finally, the absorbance was measured at 442 nm against the blank solution (Hauser and Bradley, 1966) using double beam UV- visible spectrophotometer (Systonics UV-VIS spectrophotometer 117) and the concentration empirically calculated considering 1.0 mg of O_3 per milliliter of absorbing solution generates 2.75 mg of pyridine - 4 - aldehyde per milliliter of absorbing solution. A precision of ± 1 % and a sensitivity of 0.0 – 3.65 µg of O_3 per milliliter of absorbing solution were obtained. To minimize sampling and analytical error, each method was calibrated before the measurement of collected samples.

3.2: Micrometeorology and biosphere - atmosphere O_3 exchange flux:

Meteorological variables (temperature, wind speed and relative humidity) related to this study were simultaneously recorded using portable weather monitor (Model: Davis 7440) and the data was used to calculate other micrometeorological indices like friction velocity (u*) and roughness height (Z_o). Biosphere - atmosphere O_3 exchange flux (F_{O3}) was calculated using the following relation (Barrett, 1998):

$$F_{O3} = V_C \Delta\chi.$$

Where, $\Delta\chi$ = difference of mixing ration of O_3 between 10 and 20 m height and V_C = exchange velocity which is defined as $1/ (r_a + r_s)$ [Where, r_a = aerodynamic resistance and r_s = surface layer resistance]. Negative flux indicates net transfer from the atmosphere to the biosphere and vice versa. Storage rate of O_3 during stable condition in the forest atmosphere was computed as follows (Fowler and Duyzer, 1989): ΔO_3 (storage) = $\partial C/ \partial t (Z_2 - Z_1)$.

4. Results and discussion:

4.1 Seasonal variation of O_3 mixing ratio in forest atmosphere:

Seasonal variations of O_3 mixing ratio over the forest atmosphere were found to be very clear and systematic. O_3 mixing ratios at 10 m and 20 m heights over the forest atmosphere ranged between 14.66 ± 1.88 to 37.90 ± 0.91 and 19.32 ± 6.27 to 39.80 ± 10.13 ppbv, respectively; having maximal premonsoon and minimal monsoon, periods. The concentrations measured in this mangrove forest environment were within the range of that reported by Wolfe et al., 2011 for forest ecosystems. The maximal premonsoon O_3 mixing ratio may be attributed to presence of favorable conditions for atmospheric O_3 formation like high temperature, high intensity of solar radiation and sufficiently high mixing ratio of NO/NO_x (5.23 ± 0.7 ppbv; Ganguly et al., 2009). A very similar phenomenon was previously reported by Naja and Lal, 2002. Moreover, during premonsoon there is also the enhanced possibility of O_3 transport from the stratosphere resulting significant enrichment of atmospheric O_3 mixing ratio in forest atmosphere (Reddy et al., 2010). In contrast to premonsoon, minimal monsoon O_3 mixing ratio may be due to insufficient sunlight for photolysis of O_3 precursor species as well as massive rainfall promoting wet deposition of O_3

on water droplets in this tropical forest ecosystem (Tarasova et al., 2003).

4.2 Diurnal variation and changes of O_3 concentration during daytime/nighttime:

The diurnal variation of O_3 in the mangrove forest atmosphere is characterized by higher mixing ratios during daytime (14.36 – 54.99 and 15.40 – 49.35 ppbv for 10 m 20 m heights, respectively) compare to nighttime (2.18 – 32.79 and 6.69 – 33.78 ppbv for 10 mand 20 m heights, respectively). On annual basis daytime O_3 mixing ratio was 1.69 times higher than nighttime. During daytime presence of intense solar radiation promotes NO_2 photolysis rate in the forest atmosphere producing atomic oxygen in an energetically exited state. In the next step of the reaction sequence, the atomic oxygen produces two OH radicals which in turn favor photochemical production of O_3 in the atmosphere (Crutzen et al., 1995). Moreover, Seinfeld and Pandis, 1998 reported significant photo-production of O_3 from oxidation of natural and anthropogenic hydrocarbons, carbon monoxide (CO), and methane (CH_4) by hydroxyl radical in the presence of sufficient amount of NO_x. In addition to this chemical transformation, during daytime due to convective heating there occurs downward transport of O_3 from upper atmosphere enriching O_3 mixing ratio in the lower atmosphere of this tropical mangrove forest to a considerable level (Lal et al., 2000). The low nighttime O_3 concentrations principally may be attributed to the absence of NO_2 photolysis. Moreover, formation of night inversion layer and a rapid reaction between O_3 and NO_x titration during nighttime may result a steady decrease of O_3 mixing ratio in this tropical forest atmosphere (Tyson et al., 1998). In order to compute increase rate of atmospheric O_3 from nighttime to daytime we have divided the total 24 hours time span as 07:00 - 19:00 h as daytime and 19:00 - 07:00 h as nighttime. The change of O_3 concentration from nighttime to daytime varied between 0.57 – 2.07 and 0.70 – 1.41 ppbv hr^{-1} at 10 m and 20 m height, respectively (table – 1); having an annual average of 1.15 ppbv hr^{-1}. The O_3 increment rate calculated for this site was in the range of that reported by Reddy et al., 2010 at Anantapur, South India. Storage rate of O_3 between 10 m and 20 m heights of the forest atmosphere varied between 9.34 x 10^{-5} to 1.54 x 10^{-3} µg m^{-2} s^{-1} with an annual average of 9.06 x 10^{-4} µg m^{-2} s^{-1}.

Table – 1: Average O_3 mixing ratios at Sundarbans mangrove forest during nighttime (19:00–07:00 h) and daytime (07:00– 19:00 h) and its increase rate for the study period.

Seasons	Height (m)	$[O_3]_{daytime}$ (ppbv)	$[O_3]_{Nighttime}$ (ppbv)	Increase O_3 rate (ppbv/hr)
Premonsoon	10	45.39 ± 7.27	29.46 ± 3.82	1.33
	20	41.98 ± 7.72	33.62 ± 11.55	0.70
Monsoon	10	16.52 ± 2.43	9.70 ± 3.26	0.57
	20	24.43 ± 2.17	14.21 ± 4.18	0.85
Postmonsoon	10	37.40 ± 7.39	12.57 ± 11.59	2.07
	20	37.81 ± 8.81	20.90 ± 10.29	1.41

4.3 Impact of micrometeorology on atmospheric O_3 mixing ratio:

Meteorology plays an important role in production and transportation of O_3 in the forest atmosphere. As a result, substantial variations in meteorological conditions can exert such a large impact on atmospheric O_3 concentrations. Seasonal variations of micrometeorological parameters are presented in table – 2. Temperature at 10 m height of the forest atmosphere was varied between 17.34 ± 4.09 and 30.34 ± 0.91^oC being maximal premonsoon and minimal postmonsoon periods. Following same trend of seasonal variation temperature at 20 m height over the forest atmosphere was varied between 16.17 ± 1.80 and 29.73 ± 1.13^oC.The ratio between air temperature at 10 m and 20 m height was computed as 1.04:1, indicating higher temperature in 10 m height compare to 20 m. This may be attributed to dry adiabatic lapse rate, which states that adiabatic expansion of a parcel of air as it rises; air raised to higher altitudes has a lower temperature than the air of the same composition and initial temperature at lower altitude. In order to evaluate the influence of air temperature on atmospheric O_3 mixing ratio a simple regression analysis was done between these two variables assessing different functional, linear, multiplicative, exponential and reciprocal dependencies. Statistical analysis revealed that these two variables were best fitted by the following exponential equation as follows (Fig.2):

$$[O_3] = 0.477\ e^{0.1498T}\ (R^2 = 0.41,\ n = 22)$$

The correlation coefficient explains 41% variability between these two dependent and independent variables; indicates partial impact of air temperature or indirectly solar radiation on variation of atmospheric O_3 mixing ratio in this tropical mangrove forest atmosphere. The relationship between O_3 concentration and temperature can be explained on theoretical grounds. High temperature promotes propagation rate of the radical chain in the atmosphere (Ruiz - Sua´rez et al., 1995) producing higher O_3 in the forest atmosphere.

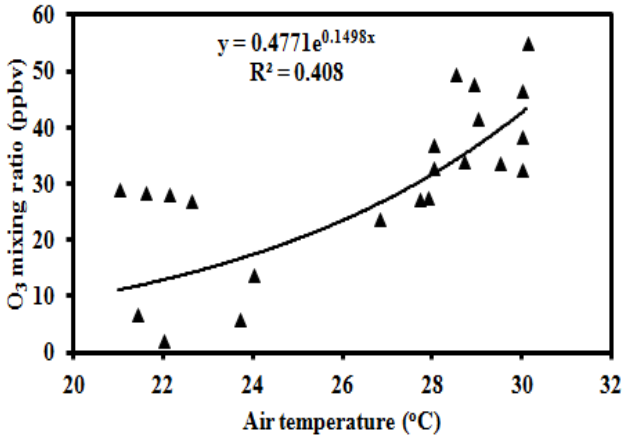

Fig.2: *Scattered plot between O_3 mixing ratio and air temperature*

Wind velocity during the survey period varied between 0.41 ± 0.36 and 1.32 ± 1.11 ms^{-1} having maximal monsoon and

minimal postmonsoon periods. Following same trend for seasonal variation average wind velocity in 20 m height in the forest atmosphere was 1.40 times higher than 10 m height.

Table – 2: Seasonal variation of O_3 mixing ratio and other micrometeorological parameters over Sundarbans mangrove forest atmosphere.

Parameters	Height (m)	Premonsoon	Monsoon	Postmonsoon
O_3 mixing ratio	10	37.90 ± 0.91	14.66 ± 1.88	25.60 ± 4.89
(ppbv)	20	39.80 ± 10.13	19.32 ± 6.27	29.36 ± 12.66
Air temp (°C)	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	10	0.70 ± 0.42	1.32 ± 1.11	0.41 ± 0.36
velocity(ms^{-1})	20	0.95 ± 0.44	1.64 ± 1.37	0.80 ± 0.88
Humidity (%)		86.75 ± 2.60	78.03 ± 17.31	74.79 ± 2.55
u* (ms^{-1})		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

It is known that there is a clear relationship between ambient air quality and wind speed and wind direction. Duenas et al., 2002 reported the influence of wind speed and wind direction for the dispersion and transport of O_3 and its precursors from their emission sources which insisted us to carry out a statistical analysis between O_3 concentration and respective wind velocity of the study site (Fig.3). The relationship between atmospheric O_3 mixing ratio and wind velocity (V) was best fitted with the following regression equation as follows:

$$[O_3] = 17.565 \ln V + 33.76 \ (R^2 = 0.50, n = 21)$$

The equation explains 50% variability between these two parameters indicating moderate impact of wind velocity on distribution of atmospheric O_3 in this tropical forest atmosphere by the process of dispersion or transportation. The reason for this partial influence may be attributed to insufficient wind dynamics and local wind circulation patterns that could not make any alteration on the dispersion and transportation of surface O_3. A similar phenomenon was noticed by Elampari et al., 2011 at tropical semi – urban site, Nagercoil, India.

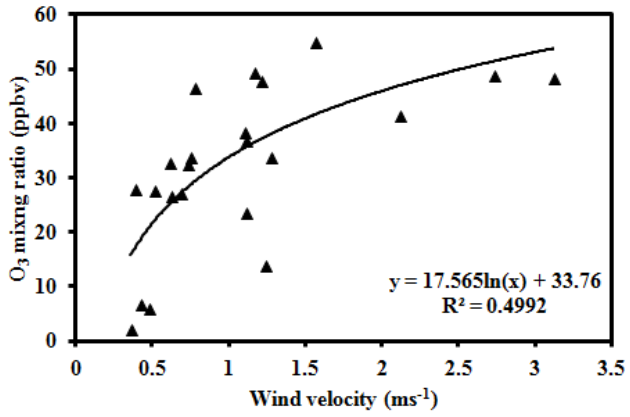

Fig.3: *Scattered plot between O_3 mixing ratio and wind velocity*

Relative humidity during the observation period varied between 74.79 ± 2.55 and 86.75 ± 2.60 % being maximal premonsoon and minimal postmosnoon periods. Atmospheric O_3 mixing ratio was best fitted with relative humidity (H) of the study site with the following regression equation as follows (Fig.4):

$$[O_3] = - 1.0645 H + 116.46 \ (R^2 = 0.14, n = 21)$$

The correlation coefficient indicates insignificant negative correlation between these two variables; indicates enhancement of photo-chemically O_3 removal pathway with increment of percentage of relative humidity in the atmosphere. A similar correlation was previously reported by Elampari et al., 2011. Values of other micrometeorological indices like friction velocity (u*) and roughness height is presented in table – 2.

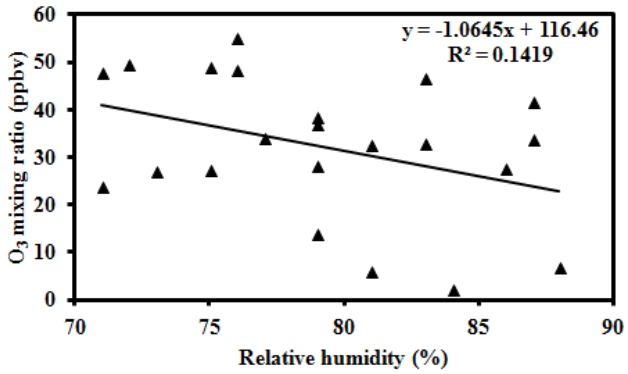

Fig.4: *Scattered plot between O_3 mixing ratio and relative humidity*

4.4 Photolysis frequency of O_3 and computation of atmospheric OH radical concentration:

From hourly deviation of solar zenith angle (x) in this tropical mangrove forest photolysis frequency of O_3 [$J(O^1D)$] was computed as follows (MCM version 3):

$$J(O^1D) = 6.073 \times 10^{-5} \cos x^{1.743} \exp(-0.474 \sec x)$$

The value of $J(O^1D)$ was computed between 8.54×10^{-8} - 3.58×10^{-5}, 1.14×10^{-7} – 3.71×10^{-5} and 2.21×10^{-12} – 1.72×10^{-5} s^{-1} for premonsoon, monsoon and postmonsoon, respectively; having an average of 1.32×10^{-5} s^{-1}. From the values of $J(O^1D)$, OH radical concentration in this forest atmosphere was computed using empirical equation ($[OH] = a\ J(O^1D)^b$) (Ehhalt and Rohrer, 2000) and the value of 'a' (1.77×10^{10} s cm^{-3}) and 'b' (b = 0.68) were taken from Berresheim et al., 2003. Using the empirical relation OH radical concentration in this forest atmosphere was varied between 2.76×10^5 – 1.68×10^7, 3.37×10^5 – 1.72×10^7 and 2.10×10^2 – 1.02×10^7 molecules cm^{-3} for premonsoon, monsoon and postmonsoon, respectively (Fig.5); having an average of 7.40×10^6 molecules cm^{-3}.

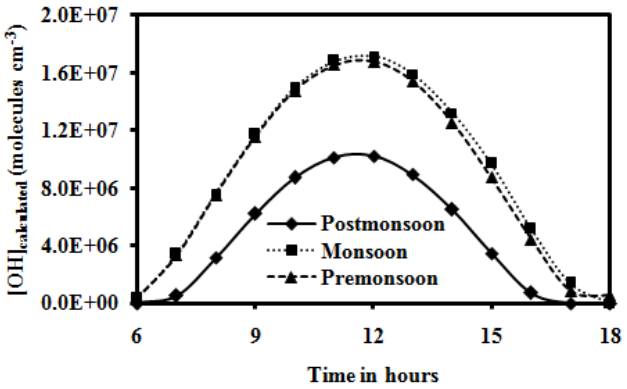

Fig.5: *Diurnal variation of OH radical concentration at 10 m height in mangrove forest*

4.4 Biosphere - atmosphere O_3 exchange flux in forest ecosystem:

Comparing vertical distribution of O_3 in the forest atmosphere, it was evident that average O_3 mixing ratio at 10 m height was 13.2 % lower than 20 m height; induces biosphere – atmosphere O_3 exchange in the mangrove forest atmosphere depending upon micrometeorological conditions of the study site. Biosphere – atmosphere O_3 exchange fluxes in this tropical mangrove forest atmosphere varied between – 0.675 to – 0.197 µg m^{-2} s^{-1} (Fig.6); having maximal premonsoon and minimal monsoon periods. Annual average biosphere - atmosphere O_3 exchange flux was – 0.441 µg m^{-2} s^{-1}; indicates the ecosystem acts as a net sink for atmospheric O_3 during the survey period.

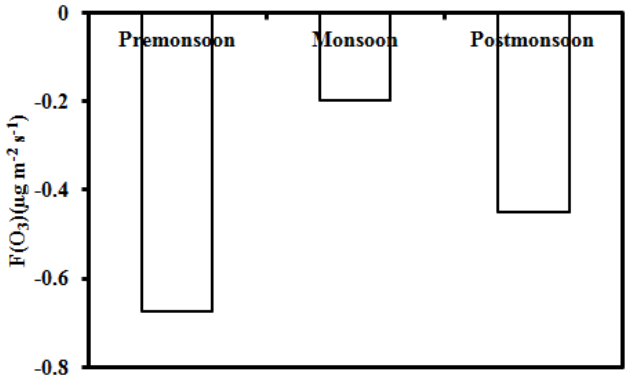

Fig.6: *Seasonal variation of biosphere – atmosphere O_3 exchange flux in mangrove ecosystems.*

The sink of atmospheric O_3 may be explained by considering physical as well as biological activities operating in the forest ecosystem. The biological activity mainly involves O_3 uptake through leaf stomata and the fact has been reported previously by very few researchers (Kozlowski et at., 1991). Moreover, aperture of the plant leaf stomata being strongly correlated with air temperature which insisted us to carry out a statistical analysis (using MINITAB version 17) between air temperature (T) and biosphere – atmosphere O_3 flux (F_{O3}). These two variables were best fitted by second order polynomial equation as given below:

$F_{O3} = 1.44 - 0.153\ T + 0.00325\ T^2$ (R^2 = 59.3%, F = 8.73, p = 0.005, n = 15)

The equation revealed significant correlation between dependent and independent variables with 59.3% variability indicating significant influence of air temperature on variability of O_3 exchange flux in this mangrove forest environment. However, mangrove and terrestrial plants stomatal physiology might differ in their stomatal response to O_3 dynamics because of high salt stress on the biochemical reaction system in mangroves. Among all the physical processes operating in this tropical forest ecosystem, dry deposition of O_3 on mangrove vegetation, water other material is the most active pathway for removal of O_3 from regional atmosphere. Average compensation point (where emission balances deposition i.e. net biosphere-atmosphere O_3 flux is zero) for O_3 in this subtropical mangrove forest was calculated to be 3.966 ppbv. Extrapolating the average biosphere – atmosphere flux rate over entire forest surface area, the ecosystem acts as a sink of 58.4Gg O_3 annually; indicates significant response of this mangrove forest towards regional atmospheric O_3 budget as well as climate change.

5. Conclusion:

Distribution of O_3 in the forest atmosphere was partially regulated by micrometeorological processes operating in the atmosphere. Average mangrove biosphere – atmosphere O_3 exchange flux was – 0.441 µg m^{-2} s^{-1} and fluxes were significantly regulated by air temperature. Total uptake of O_3 in this mangrove forest ecosystem was 58.4Gg on annual basis indicating significant contribution of Sundarbans mangroves towards reducing burden of atmospheric O_3.

6. Acknowledgment:

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