Biosphere-atmosphere exchange of NO_x in the tropical mangrove forest

D. Ganguly,[1] M. Dey,[1] S. Sen,[2] and T. K. Jana[1]

[1] Biosphere-atmosphere exchange of NO_x at the Sundarban mangrove forest along the northeast coast of the Bay of Bengal, India, showed uptake rates of -0.84 to -1.63 ng N m^{-2} s^{-1} during the day and both uptake and emission rates of -0.36 to 5.19 ng N m^{-2} s^{-1} during the night from September to February. However, during the period from March to August, NO_x emission ranged between 0.34 and 2.13 ng N m^{-2} s^{-1} and 0.88 and 3.26 ng N m^{-2} s^{-1} in daytime and nighttime, respectively. During the postmonsoon period, NO_x uptake could be attributed to mangrove stomatal activity during the day. Mangroves absorbed nitrogen from both the soil and the atmosphere. Seasonal and diurnal variability of NO_x and O_3 is partly due to plant growth in the postmonsoon period. In addition to the NO_x-O_3 photochemical cycle, stomatal uptake of NO_x could also be an important process for keeping a low-ozone state at the land-ocean boundary of the northeast coast of the Bay of Bengal.

1. Introduction

[2] To address net nitrogen biosphere-atmosphere exchange, different nitrogen forms, namely, NO_x, N_2O, and NH_3, need to be considered. Quantification and understanding of individual processes controlling the nitrogen cycle are also necessary [*Sutton et al.*, 2007]. In the tropical rain forest region a low-ozone state of the troposphere can be achieved by tight interaction of biological, chemical, and physical processes that allows efficient turnover of nitrogen and prevents emission to the atmosphere [*Andreae*, 2002]. Nitric oxide (NO) is produced during nitrogen turnover that accompanies the breakdown of biological matter in soils; the resulting gas can then escape into the air layers over the soil. During its escape, a part of the NO can react with ozone to form NO_2, which can be efficiently deposited on plant surfaces and may be taken up through stomata and used in protein synthesis and plant growth. Such a process limits the amount of NO emitted to the atmosphere and contributes to ozone formation. The enzyme nitrate reductase (NR), occurring either in the root or in the leaf, could catalyze the reduction of nitrate assimilated from the ambient medium to nitrite using the natural electron donor NADH. In shifting from the use of root NR to shoot NR, the plants are able to use NO and NO_2 from the atmosphere, even though plenty of nitrate is available to the roots [*Hufton et al.*, 1996]. *Wellburn* [1998] suggested that plants capable of uptaking NO_x could be selected for forestation to achieve a low-ozone state. Normally, NR reduces nitrate to nitrite, but nitrite may be further reduced to NO, which can be emitted to the atmosphere through leaf stomata [*Crawford*, 2006]. Tropical deforestation and land use change enhances NO_x emission, with a consequence of transition from low- to high-ozone states [*Andreae and Crutzen*, 1997]. In the tropical mangrove forest with its tight water management and low evapotranspiration [*Barr et al.*, 2005; *Ganguly et al.*, 2008], there is a better scope for the plants to use shoot NR than root NR. This study deals with four main questions: (1) Are mangrove forests in the Sundarbans capable of uptaking NO_x through stomatal assimilation? (2) Does assimilation of NO_x vary during premonsoon, monsoon, and postmonsoon seasons? (3) Does assimilation of NO_x vary during day and night? (4) How does NO_x (gas) assimilation by mangrove forests contribute to the reduction of O_3 in the atmosphere?

2. Study Area

[3] The total area of the Indian Sundarban mangrove forest is 9630 km^2, out of which 4264 km^2 is under reserved forest in the estuarine phase of the river Ganges. It is the largest delta in the world (World's Heritage Site, http://whc.unesco.org/en/list/452) and is a unique bioclimatic zone for its biodiversity of mangrove flora and fauna, both on land and in water, at the land-ocean boundary of the Bay of Bengal ($20°32'-20°40'$N, $88°05'-89°$E). Measurements were carried out at two sites: station 1 at Sajnekhali Island in the reserve forest area at a distance of about 65 km north from the coast and station 2 at Lothian Island in the confluence of the Saptamukhi River and the Bay of Bengal (Figure 1). The proximity of the Kolkata metropolis to station 1 could influence the forest air quality. Mangroves, namely, *Avicennia officinalis*, *Avicennia alba*, *Avicennia*

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[1]Department of Marine Science, University of Calcutta, Calcutta, India.
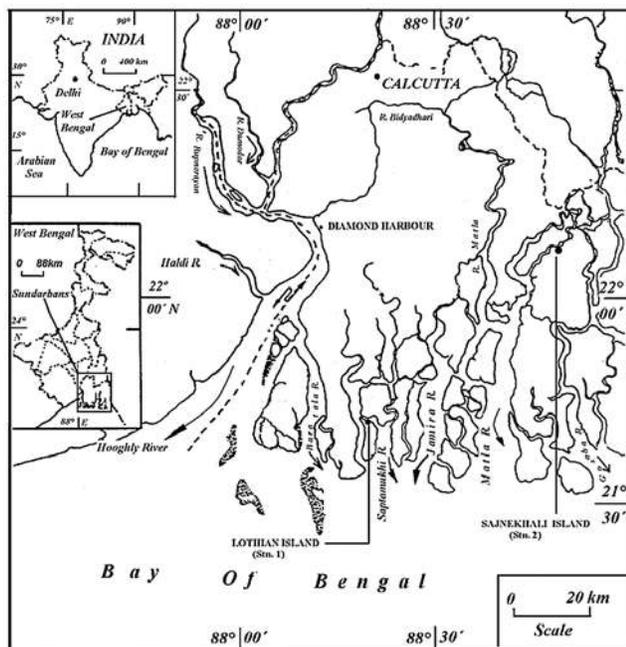[2]Department of Chemistry, University of Calcutta, Calcutta, India.

Figure 1. Map showing the station locations.

marina, and *Aegiceros* sp., are the dominant species found on both islands. *Excoecaria agallocha* and *Heritiera fomes* are also found on these two islands. Mangrove plants rarely exceed 10 m in height, and the over-forest trajectory of the wind (fetch) is about 15 km.

3. Material and Methods

[4] Observations were made in every month during the new moon at 3 h intervals for 24 h at each site, covering three seasons, premonsoon (March−June), monsoon (July−October), and postmonsoon (November−February), during 2006−2007. For micrometeorological and atmospheric NO_x-O_3 measurement, a tower of 25 m height was placed in the deep forest at both sites with computerized weather monitoring sensors (Davis 7440) mounted at 10 and 20 m to measure wind, temperature, and humidity. A sampling train was assembled in duplicate for each NO_x and ozone measurement by connecting in series the prefilter and holder, absorber, a calibrated rotameter, and an air pump (Technovarian AS2). Two sets were run concomitantly at 10 and 20 m. For NO_x, air was bubbled through 25 mL of an absorbing solution made of 0.1% sodium arsenite solution in 0.4% sodium hydroxide. After a 3 h run (1 L min^{-1}) the contents were quantitatively transferred and mixed with H_2O_2 (0.024%), sulphanilamide (2%), and N-(1-naphthyl)-ethylenediamine dihydrochloride (0.1%). After a 10 min color development interval, the absorbance was measured at 540 nm against the blank solution [*Jacobs and Hochhieser*, 1958; *APHA Intersociety Committee*, 1977]. Standard solutions of concentrations ranging between 0.04 and 2.0 μg NO_2 mL^{-1} were used for calibration, and a sensitivity of 0.002−0.100 ppmv NO_x was achieved. Relative error of accuracy for NO_x estimation was ±3.62%. For ozone, air was 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 a rate of 0.5 L min^{-1}. After a 2 h run 10 mL of the solution was pipetted into a test tube. One milliliter of the color-developing reagent (0.2% aqueous solution of 3-methyl-2-benzothiazolinone hydrazone hydrochloride) was then added, and the mixture was heated in a boiling water bath for 20 min and cooled. The absorbance for yellow-colored azine formation was then measured at 442 nm against the blank solution [*Hauser and Bradley*, 1966]. It was empirically determined that 1.0 μg of ozone per milliliter of absorbing solution generates 2.75 μg of pyridine-4-aldehyde per milliliter of absorbing solution. 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. A precision of ±1% and a sensitivity of 0.0−3.65 μg of ozone per milliliter of absorbing solution were obtained. Nonaerated blanks were prepared from absorbing solution that stood in the field for the same length of time as the absorbing solution used in sampling. To minimize sampling and analytical error, each method was calibrated before the measurement of samples. Micrometeorological data were considered as 3 h blocks for mean value to match the trace gas measurement data. To examine the role of soil inorganic nitrogen and leaf nitrate reductase for protein synthesis in the leaf, total inorganic nitrogen in the soil and leaf nitrate reductase activity (LNRA) were measured. Leaf samples were collected from 10 m heights. Total leaf protein was estimated by extracting 500 mg of the sample with a phosphate buffer. The mixture was centrifuged, and the supernatant was used to estimate protein by Lowry's method [*Plummer*, 1971]. For total inorganic nitrogen in soil, 30 g of soil subsample was collected from the surface (0−10 cm) and 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 overnight. After 24 h, 4 mL of the supernatant was collected for the estimation of ammonia-nitrogen (NH_4^+-N) and nitrate-nitrogen (NO_3^--N) by spectrophotometric method [*Riley et al.*, 1995].

[5] To measure LNRA, 1 g samples of leaves of different mangrove species were homogenized under ice-cold conditions using a 6 mL medium containing 1 mmol ethyl-enediaminetetraacetic acid (EDTA), 25 mmol cystine, and 25 mmol potassium phosphate buffer adjusted to a final pH of 8.8 with potassium hydroxide. The extract was centrifuged, and 0.2 mL of each extract were used for the change of NADH-dependent nitrate reduction to nitrite followed by its subsequent determination by spectrophotometric method using sulphanilamide and napthyl-ethylene-diamine reagent [*Hageman and Reed*, 1980]. LNRA was expressed as micromoles of nitrite (NO_2^-) produced per minute per milligram of leaf protein. The rate of exchange of NO_x between biosphere and atmosphere was calculated considering aerodynamic resistance (r_a), surface layer resistance (r_s), canopy resistance (r_c), and the concentration difference $\Delta\chi = \chi_{10} - \chi_{20}$ for forest cover area. With exchange velocity, V_C, defined as $1/(r_a + r_s + r_c)$, net flux, F, was calculated using the relation [*Barrett*, 1998]

$$F = V_C \times \Delta\chi.$$

Negative F indicates net uptake from the atmosphere to the biosphere, and positive F indicates emission. The confidence limit of the flux measurement was calculated using

Table 1. Seasonal Variations of Micrometeorological Parameters[a]

	Premonsoon	Monsoon	Postmonsoon
Temperature at 10 m (°C)	28.5 ± 3.47	29.5 ± 1.9	23.08 ± 4.5
Temperature at 20 m (°C)	27.9 ± 3.0	28.8 ± 2.0	22.2 ± 4.7
Wind velocity at 10 m (m s^{-1})	1.93 ± 1.40	1.28 ± 1.13	0.72 ± 0.72
Wind velocity at 20 m (m s^{-1})	2.82 ± 1.3	1.76 ± 1.45	1.7 ± 1.11
Wind direction (deg)	$135-360$	$45-135$	$270-360$
Frictional velocity (m s^{-1})	0.51 ± 0.36	0.66 ± 0.19	0.58 ± 0.29
Z_0 (m)	4.91 ± 2.31	5.77 ± 2.21	6.46 ± 2.08
Pressure (mm)	757 ± 1.36	754.1 ± 3.1	763.4 ± 1.76
Humidity (%)	81.5 ± 16.9	89 ± 11	71.4 ± 18.3
Canopy resistance (r_c) at day	117 ± 32	113 ± 5	134 ± 33
Canopy resistance (r_c) at night	191 ± 22	191 ± 6	245 ± 43

[a]Mean of station 1 and station 2 $\pm$ SD.

the relation $\bar{X} \pm ts/\sqrt{N}$ where $\bar{X}$ is the mean value, s is the standard deviation, N is the number of observations, and t is the statistical factor that depends on the number of degrees of freedom and the confidence level derived [*Christian*, 2001]. The aerodynamic resistance was evaluated from the relation [*Wesely and Hicks*, 1977]

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

where Z_0 is the roughness height and Ψc is a correction function for atmospheric stability. It serves to increase r_a for stable conditions and decrease it for unstable conditions. The equations for the correction functions are [*Wesely and Hicks*, 1977]
Stable condition

$$\Psi_c = -5(Z/L), \quad 0 < Z/L < 1$$

Unstable condition

$$\Psi_c = \exp\left[0.0598 + 0.39\ln(-Z/L) - 0.09\{\ln(-Z/L)\}^2\right],$$
$$0 > Z/L > -1.$$

The correction functions are expressed in terms of a stability parameter Z/L, 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

$$u^* = k(u_1 - u_2)/\ln(Z_2/Z_1),$$

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 have an average height of 10 m) was considered [*Panofsky and Dutton*, 1984]. The scale length, L, was evaluated by the use of Pasquill stability classes 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 the 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.

[6] Surface layer resistance, r_s, for forest cover was calculated using the following relations [*Wesely and Hicks*, 1977]:

$$kB^{-1} = 2(K/Dc)^{2/3}$$

and

$$r_s = B^{-1}/u^*,$$

where B^{-1} is the transfer function, k is the Von Karman constant, K is the thermal diffusivity of air, and Dc is the molecular diffusivity

$$Dc = D_0(T_2/273)^{1.5},$$

where T_2 is the temperature at 20 m height and D_0 (cm^2 s^{-1}) is 0.115 for NO$_x$ and 0.124 for O$_3$.

[7] For canopy resistance, r_c, the following relation was used:

$$r_c = \{[\ln(z - d) - \Psi_c]/ku^*\} - (r_a + r_s),$$

where d is the zero plane displacement, being in the range 0.7–0.8 of mean plant height [*Panofsky and Dutton*, 1984; *Hicks*, 1989].

[8] *Parrish et al.* [1987] extensively intercompared the gradient method with the enclosure technique, and an excellent agreement between these two independent methods was obtained over a three-order magnitude range of soil NO$_x$ emission. The photo dissociation rates for NO$_2$ (J$_{NO_2}$) were computed at station 2 for the variation of solar zenith angle, α, with time ($90°-45.51°$ in December and $78.54°-3.99°$ in July) using the relation [*Parrish et al.*, 1983]

$$J_{NO_2}(\alpha) = 0.1305\ \exp(-0.36\sec\alpha).$$

Stepwise regression analyses were done using the Minitab (version 4.0) statistical package. The horizontal gradients in concentrations of NO$_x$ and O$_3$ between the two stations were used to calculate the advection error, and their vertical gradient with time over the height interval 10–20 m was considered as a storage error. The errors introduced through advection, storage, and photolysis of NO$_x$ were estimated. Advection error ranged from 0.07% to 1.8% for NO$_x$ and from 0.06% to 0.48% for O$_3$. Storage error ranged from 0.87% to 4.06% for NO$_x$ and from 0.23% to 1.93% for O$_3$. Data for flux measurements were considered only when the coefficient of variation was below 1% for air temperature and below 5% for wind velocity during the 3 h of each sampling.

4. Results and Discussion

[9] Annual movement of the Intertropical Convergence Zone in this part of the world produces significant changes in micrometeorological parameters throughout the year because of differential temperature and frictional length in different seasons (Table 1). Mean canopy resistances of 134 ± 33 s m^{-1} for the day and 245 ± 43 s m^{-1} for the night were found during postmonsoon with minimum humidity
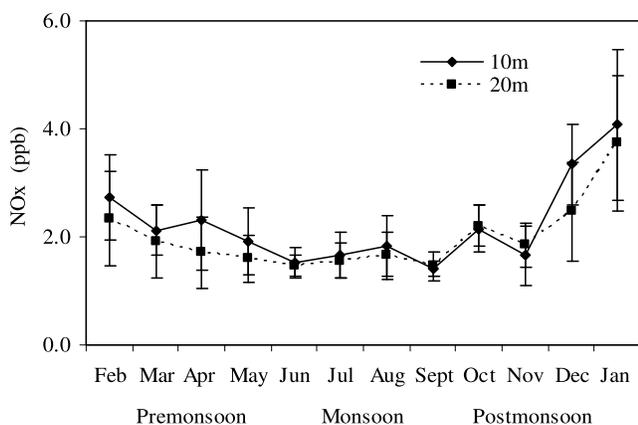
Figure 2. Monthly variation of mean atmospheric NO_x at 10 and 20 m height. Vertical bars represent 95% confidence limit.

and temperature (Table 1). During the postmonsoon season, temperature and humidity were significantly different relative to premonsoon ($p = 0.067$) and monsoon ($p < 0.001$) seasons. *Eugster and Hesterberg* [1996] observed median minimum stomatal resistance of 120 s m^{-1} for moist conditions and a maximum of 50 s m^{-1} for a litter meadow at a rural site in the Swiss plateau with relatively dry soil. *Hargreaves et al.* [1992] reported minimum canopy resistance of 100 s m^{-1} over a drained marshland pasture in southeast England. A diurnal maximum temperature difference of 13.0°C was observed in December, and a minimum of 3.9°C was observed in June. During premonsoon and postmonsoon seasons, inversion of temperature, i.e., temperature increase with altitude, was observed in the night between 0000 and 0400 LT.

[10] Progressive decrease of NO_x was observed from a maximum of 4.34 ± 1.49 ppbv in January to a minimum of 1.57 ± 0.19 ppbv at 10 m in the month of September (Figure 2). During the period of September to February, the biosphere-atmosphere NO_x exchange rates of -0.84 to -1.63 ng N m^{-2} s^{-1} in the day and -0.36 to 5.19 ng N m^{-2} s^{-1} in the night were observed. However, during the period of March to August, the ecosystem showed NO_x emission without any uptake and ranged from 0.34 to 2.13 ng N m^{-2} s^{-1} in the day and from 0.88 to 3.26 ng N m^{-2} s^{-1} in the night (Figure 3).

[11] Photolysis rates of $0.01-0.28$ ng N m^{-2} s^{-1} could result in a 5.2% error for the NO_x flux estimate. Relative uncertainties introduced by these three processes in the NO_x flux measurement were found to be $5.12\%-6.68\%$. Diurnal variation of NO_x exchange flux during the postmonsoon season is given in Figure 4. The data showed increased NO_x uptake with increasing solar radiation in the day followed by its emission in the night, which could be attributed to stomatal uptake in the daytime. The stomata close during the night, which could reduce NO_x uptake [*Hill*, 1971]. Mangrove soil bacterial influence on NO_x emission was expected to be low during the nighttime diurnal minimum temperature compared to the daytime temperature [*Williams et al.*, 1988]. From long-term flux measurements of NO_x over moorland in Scotland, *Fowler et al.* [1998] suggested that removal of NO_x could be regulated to some extent by soil production, but the major sink for NO_2 was owing to stomatal uptake. *Hargreaves et al.* [1992] observed a net sink for atmospheric NO_x in the drained marshland pasture in southeast England. NO_x emission and high NO_x in nighttime in the present study are mainly because of the closing of mangrove leaf stomata. *Ganguly et al.* [2008] observed seasonality in daytime photosynthetic CO_2 sequestration over the Sundarban mangrove forest with a minimum rate of 22.7 μm m^{-2} s^{-1} during monsoon season and a maximum rate of 225 μm m^{-2} s^{-1} during postmonsoon season (February). Annual variation of CO_2 emission in the night ranged from 52.3 to 95.4 μm m^{-2} s^{-1}. Net sink strength for CO_2 was found to be 206 Gg d^{-1}. This mangrove ecosystem showed a sink for NO_x in postmonsoon when photosynthetic CO_2 uptake was the highest. Seasonal variation of total inorganic nitrogen in the sediment (TIN) and atmospheric NO_x showed greater concentration in the postmonsoon season (Table 2).

[12] The significance of leaf protein was tested by multiple regression analysis. The dependent variable was leaf protein, and the independent variables were TIN, NO_x flux (F_{NO_x}), and LNRA. Statistical analysis revealed significant correlation between leaf protein and independent variables
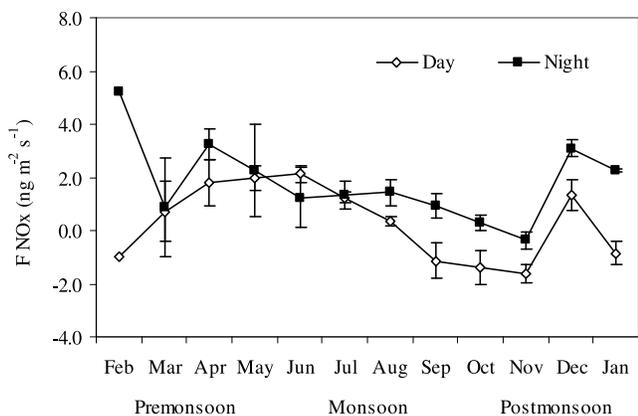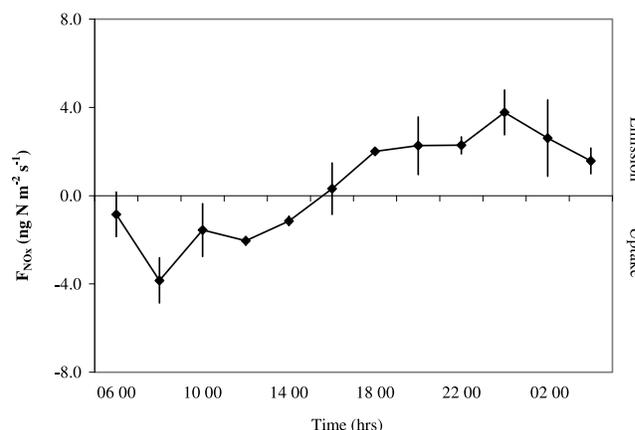

Figure 3. Monthly variation of mean NO_x exchange flux in the daytime and nighttime ($n = 12$ for one diurnal cycle in each month observed at two stations). Vertical bars represent 95% confidence limit.

Figure 4. Diurnal variation NO_x emission and uptake flux in the postmonsoon period.

Table 2. Seasonal Variation of Leaf Protein, Total Inorganic Nitrogen in the Mangrove Sediment, Leaf Nitrate Reductase Activity, and NO_x and O_3 in the Air[a]

	Premonsoon	Monsoon	Postmonsoon
P (mg/g dry weight)	150.5 ± 10.4	177.9 ± 12.4	151.2 ± 1.4
TIN (μg g^{-1})	2.91 ± 0.48	3.49 ± 0.28	3.99 ± 1.58
LNRA (μmol NO_2 m^{-1} (mg leaf protein)$^{-1}$)	0.204 ± 0.004	0.213 ± 0.002	0.203 ± 0.009
NO_x at station 1 (ppbv)	6.0 ± 1.73	3.9 ± 0.9	9.36 ± 3.2
NO_x at station 2 (ppbv)	5.23 ± 0.7	3.58 ± 0.45	6.61 ± 1.72
O_3 at station 1 (ppbv)	32.99 ± 5.3	23.87 ± 5.91	31.35 ± 2.31
O_3 at station 2 (ppbv)	24.32 ± 3.9	13.03 ± 5.1	21.03 ± 2.48

[a]P, leaf protein; TIN, total inorganic nitrogen in the mangrove sediment; LNRA, leaf nitrate reductase activity.

tested ($R = 0.92$, $p = 0.016$) with 85.2% explained variability. Stepwise regression analysis of data (Table 3) showed that soil inorganic nitrogen could explain only 10.3% of the variation of leaf protein compared to 44.1% and 30.8% by F_{NO_x} and LNRA, respectively. Once NO_x was taken up into the apoplast, NO_2 was dissolved to form NO_3^- and NO_2^- [*Lea et al.*, 1994], followed by their reduction to NH_4^+, which could be assimilated into amino acids via the normal enzymatic pathways: nitrate reductase, nitrite reductase, and the glutamine synthetase and glutamate synthase cycle [*Stulen et al.*, 1998]. *Muller et al.* [1996] observed a negative feedback effect of atmospheric NO_2 uptake on nitrogen uptake by the roots of *Picea abies* (L.) Karst., and the contribution of atmospheric nitrogen was found to be 10%–15% toward the total plant nitrogen budget.

[13] In measurements of NO_2 uptake by a wide range of conifer and broadleaf tree species as well as agricultural plants, *Rogers et al.* [1979] found that its uptake was favored by its rapid reaction with apoplast components and was controlled by diffusive resistance of the stomatal aperture. NO_2 uptake by external (cuticular) surfaces of vegetation was confirmed with a deposition velocity of 1 mm s^{-1} for canopies of vegetation with closed stomata [*Rogers et al.*, 1979; *Hanson and Lindberg*, 1991; *Thoene et al.*, 1991]. *Hargreaves et al.* [1992] showed no NO_2 uptake at night, but daytime deposition velocities were consistent with stomatal uptake with negligible mesophyll resistance. The data on the uptake by plants at higher concentrations (∼100 ppbv NO_2) indicated an uptake on the surface of the leaves in addition to the flux through stomata. The ambient concentration leading to no net biosphere-atmosphere exchange (uptake rate is equal to emission rate) is known as the compensation point [*Sutton et al.*, 1998], and *Johansson* [1987] observed a NO_x compensation point in
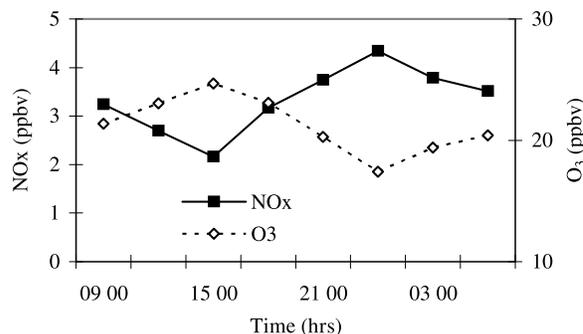
the range from 0.1 to 5 ppbv for pine forests. In this study, the NO_x compensation point was calculated to be 4.68 ± 1.34 ppbv for the Sundarban mangrove forest. However, mangrove and terrestrial plants' stomatal physiology might differ in their stomatal response to NO_x dynamics because of high salt stress on the biochemical reaction system in mangroves. Atmospheric NO_2 uptake played a significantly higher role on leaf protein content compared to soil inorganic nitrogen in the Sundarban mangrove ecosystem.

[14] A representative graph for the diurnal variation of NO_x and O_3 at station 2 on 15 February 2007 (postmonsoon) over a 24 h period is illustrated in Figure 5. The diurnal cycle showed a decrease of NO_x in the daytime followed by an increase during the night. A reverse trend was observed for O_3. A similar pattern was observed during premonsoon and monsoon periods. Mangrove stomatal uptake was the main sink for NO_x and NO_x-driven O_3 production, i.e., photolysis (0.01 and 0.2875 ng N m^{-2} s^{-1}) could account for 5.2% of the total sink rate for NO_x. A simple photochemical box model [*Fehsenfeld et al.*, 1983] for net production of O_3 attributable to the NO_x-O_3 photochemical cycle in the presence of additional oxidants other than O_3 predicted that for NO_x levels between 1 and 10 ppbv subjected to one diurnal radiation, the O_3:NO_x volume ratio in the late afternoon was expected to vary between 5 and 80. *Parrish et al.* [1986] observed reduction of the O_3:NO_x volume ratio due to the presence of an oxidant other than peroxy radicals that led to O_3 consumption and a sizable imbalance in photostationary states accompanied by no increase in the O_3 mixing ratio. The O_3:NO_x volume ratio was found to vary between 4 and 22, with the maximum value in May (premonsoon), indicating the occurrence of terpene and isoprene types of hydrocarbon and their rapid oxidation by O_3 and OH [*Stroud et al.*, 2005]. Seasonal variation of the mixing ratio of O_3 in the mangrove forest was found to be between 13.03 and 24.32 ppbv (Table 2), being lower in magnitude relative to the open ocean. *Mandal et al.* [1999] observed ozone-mixing ratios of the order of 30–60 ppbv over the Indian Ocean (15°N–20°S). The observations at the tropical rain forest reflected a pristine atmospheric composition as indicated by 6 ppmv ozone [*Fan et al.*, 1990]. Ozone has been showing downward trends for decades because of the NO_x and VOC reductions (J. Schwartz, Ground level ozone trends: Facts vs. fantasy, blog commentary, 2007, http://worldclimatereport.com).

Table 3. Multiple Regression Analysis With a Stepwise Variable Selection[a]

Predictor	R^2	p	F	n
F_{NO_x} (ng N m^{-2} s^{-1})	44.1	0.051	5.53	15
LNRA (μmol NO_2 min^{-1} (mg protein)$^{-1}$)	74.9	0.016	8.96	15
TIN (μg (g dry soil)$^{-1}$)	85.2	0.016	9.62	15

[a]The dependent variable, leaf protein content (in mg (g dry leaf)$^{-1}$), is not shown. Protein (P) = $-102 - 1.86 F_{NO_x} + 1354$ LNRA $- 3.21$ TIN. The independent variables are NO_x flux (F_{NO_x}) (ng N m^{-2} s^{-1}), leaf nitrate reductase activity (LNRA) in μmol NO_2 min^{-1} (mg protein)$^{-1}$, and total inorganic N content in soil (TIN) in μg (g dry soil)$^{-1}$.

Figure 5. Diurnal variation of the atmospheric NO_x and O_3 concentrations on 15 February 2007. Time of day is the local time.

[15] *Chatterjee et al.* [2006] observed sulfate aerosol loading with a rate of 0.19 μg m^{-2} s^{-1} in January (postmonsoon) to 4.29 μg m^{-2} s^{-1} in April (premonsoon) at the land-ocean boundary condition of the Sundarban mangrove forest, and mean concentrations of water-soluble nitrate ions were found to be 1.55 ± 1.13, 1.52 ± 1.61, and 0.66 ± 1.13 μg m^{-3} in coarse, accumulation, and nucleation modes, respectively. Further oxidation of NO_2 by reaction with O_3 to form a $[NO_3\cdot]$ radical and its subsequent reaction with NO_2 to form N_2O_5, followed by its hydrolysis to HNO_3 over an aerosol surface, could also decrease the O_3 mixing ratio. *Tie et al.* [2003] observed reduction of NO_x in winter due to the N_2O_5 hydrolysis on sulfate aerosol with a decrease of O_3.

[16] Consequences on the O_3 and its precursor, NO_x concentrations, were examined in the absence of a mangrove forest. *Dutta et al.* [2009] measured nocturnal variations of NO_x in the ambient air of Kolkata (∼150 km north of the study area) at three sites and observed considerably higher NO_x in daytime (average of 18.27–48.29 μg m^{-3}) relative to nighttime (average of 9.13–35.62 μg m^{-3}) because of emissions from greater vehicular movement. *Schnell et al.* [2009] observed an increase of ozone concentrations from 10 to 30 ppbv at night to >140 ppbv before noon in rural sites (Wyoming, United States) during winter when high concentrations of O_3 precursors developed under inversion conditions of the atmosphere at night.

5. Conclusion

[17] Five major conclusions have been drawn as a result of our research.

[18] 1. During the postmonsoon period, mangroves remain active when their stomata are open during daylight and uptake of NO_2 takes place.

[19] 2. Differences in seasonal and diurnal variations between NO_x and O_3 occur during premonsoon, monsoon, and postmonsoon seasons.

[20] 3) Correlation between leaf protein, NO_x flux, and total soil inorganic nitrogen suggests that mangroves could absorb nitrogen from both the soil and the atmosphere.

[21] 4) A CO_2-induced increase in plant primary productivity may enhance soil nitrogen and phosphorus utilization, driving mangrove areas with tight nutrient budgets to nitrogen and phosphorus limitation. Environmental changes such as temperature, sea level, and rainfall are expected with rising concentrations of CO_2, and the relative importance of the CO_2 effect on NO_x uptake needs to be further assessed in the context of the impact of future climate change on mangrove environments.

[22] 5) Further, ground level O_3 is expected to rise during the 21st century, affecting plant growth and CO_2 uptake, which could exacerbate CO_2-induced greenhouse warming [*Sitch et al.*, 2007]. This study shows that mangroves could use atmospheric NO_x as a source of nitrogen other than soil and are expected to show increasing responses to rising CO_2. This could keep ground level O_3 low, with less probability that stunted plant growth would affect CO_2 absorption.

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M. Dey, D. Ganguly, and T. K. Jana, Department of Marine Science, University of Calcutta, 35 B. C. Road, Kolkata-700019, India. (tkjana@hotmail.com)

S. Sen, Department of Chemistry, University of Calcutta, 92 Acharya Prafulla Chandra Road, Kolkata-700009, India.