

Temporal variation of carbon dioxide and water vapor density over a station in west coast of Arabian Sea during sea breeze and land breeze

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ABSTRACT

Carbon dioxide (CO₂), water vapor (H₂O), wind (speed and direction) and air temperature was measured at 5 m above ground level (AGL) on a micrometeorological tower (9 m height) over Goa (15°21' N, 73°51' E), India. The observations pertaining to summer monsoon (July – September) and post monsoon (October) season of 2002 were analyzed to study the effect of surface layer stability on the variation of CO₂ and H₂O concentrations. Based on the surface wind direction, the observations were separated for sea breeze and land breeze hrs, which show that during sea breeze times the CO₂ concentration was decreasing and H₂O concentration increasing and the opposite trend during land breeze.

Key words: CO₂, water vapor, wind speed, atmospheric stability, sea breeze, land breeze.

INTRODUCTION

An increase in carbon dioxide (CO₂) concentrations in the atmosphere due to anthropogenic activities is responsible for the global warming and hence in recent years, CO₂ measurement network has been expanded globally. Recently, the CO₂ levels have gone up to a daily mean of 400 ppm in May 2013 at Mauna Loa, Hawaii (Monastersky, 2013). The CO₂ concentrations can vary from one station to other depicting a low concentration in rural sites (Patil et al., 2014) and high concentration in an urban site (Grimmond et al., 2002; Velasco and Roth, 2010). The long-term variation of atmospheric CO₂ is due to fossil fuel combustion and the change in uptake capability of the terrestrial biosphere reservoirs and the ocean (Mook, 1986), whereas the short-term variation in atmospheric CO₂ is due to the CO₂ accumulation capacity of plants during photosynthesis and release during respiration (Keeling et al., 1989; Mook, 1986; Jones et al., 1978; Ohtaki, 1985; Ohtaki and Matsui, 1982). The gas exchanges during atmosphere ocean interaction (Berner, 1999) can also lead to short term CO₂ variation over oceanic region. The amplitude of short term variation is larger than the long-term variation, therefore the study on diurnal variation of CO₂ is necessary for understanding the fluxes of CO₂ exchanged between atmosphere and terrestrial biosphere (Heimann et al., 1989) at shorter time scale. During summer, the day time reduction in CO₂ concentration is caused by photosynthetic uptake and deep convective turbulent mixing in the lower

layers of Atmospheric Boundary Layer (ABL) whereas at night the amplification of CO₂ concentration near the surface due to respiration process by plants and a shallow stable ABL (Patil et al., 2014).

Sea is normally a sink for CO₂ and a source for water vapor and so the variation of these quantities is of interest when wind blows from the sea towards the coast and vice versa. The open ocean CO₂ observations (Watson et al., 1991) indicate large spatial variability in partial pressure (Δp) of CO₂, due to surface biological factors. Also studies on ocean CO₂ show that north Indian ocean is a net sink of atmospheric CO₂ (Takahashi, 1989; Louanchi et al., 1996). Tans et al., (1990) found that CO₂ in surface waters of North Indian Ocean is richer than in the atmosphere. Sarma et al., (1998) showed that in all seasons, the partial pressure of CO₂ is higher in the surface waters than in the atmosphere of the Arabian Sea, except in the southwest monsoon. Over the land stations in India, large spatial and seasonal variability in CO₂ concentration is observed (Sharma et al., 2013, 2014). During the monsoon season (June-September) it is found that rural site is a net CO₂ sink region (Patil et al., 2014) over the Indian subcontinent. It is observed that an urban site is a source region (Grimmond et al., 2002; Velasco and Roth, 2010) for CO₂. The present study pertains to the coastal station of Arabian Sea in India. The coast is a transition region between land and ocean and of biological and physical diversity due to large temperature gradients, change in surface roughness, internal boundary layers (IBL), local sea



Figure 1. Aerial view of measurement site along with observation location at Vasco-da-Gama, Goa marked from the Google Earth view.

and land breeze circulations, air-sea exchange modulation, air bubble entrainment, presence and absence of capillary wavelets. The shallow coastal waters enhance the biological productivity, which can affect CO_2 concentrations. All these factors and their interactions make coastal micrometeorological measurements challenging (Crawford et al., 1993; Jones and Smith, 1977; Leuning et al., 1982). Hence, it is of interest to measure and study CO_2 and water vapor variations over coastal stations. In the present study, CO_2 and water vapor mass density observations were collected during summer monsoon of 2002, at Goa coast using a fast response open path infrared gas analyzer. These observations have been analyzed to study the effect of surface layer stability on the temporal variation of CO_2 . The effect of sea and land breezes on the variability of CO_2 concentrations over the coastal station has also been explored. These details and results are presented and discussed in this research article.

DATA AND METHODOLOGY

A micrometeorological tower (9 m high) was erected on the headland (58.5 m asl) in the premises of National Centre for Antarctic and Ocean Research (NCAOR), Vasco-da-Gama, Goa ($15^\circ 21' \text{ N}$, $73^\circ 51' \text{ E}$), which is ~ 25 m away from the Arabian Sea coast. Figure 1 shows the topography of the site and experimental set-up. A Sonic anemometer (Applied Technology, USA) and water vapor ($\text{H}_2\text{O}/\text{CO}_2$) analyzer (LICOR-7500, USA) was installed at 5 m height to measure the fluctuations of CO_2 , water vapor, wind components (u , v and w), wind direction and air temperature (T).

These observations sampled at the rate of 10 Hz were further averaged for 30 minutes to use in the analysis. The NCAOR buildings are ~ 150 m away towards the north direction of tower. During monsoon season, forest breeding plants and grass of about 1–1.5 m height grow over the terrain on NW–NE sector. The experimental site has a large fetch (sea) in the upwind direction. Except wind from NNE–ESE direction, the wind approaching the coast from all other directions is from the sea. Wind coming from N–ESE direction (0 – 112°) is taken as a wind from land. The details on the topography of the site, sensors on the tower and the experimental setup have been reported by Sivaramakrishnan et al., (2003).

The $\text{CO}_2/\text{H}_2\text{O}$ analyzer is a high performance, non-dispersive open path instrument used in eddy covariance flux measurements. It uses the principle of absorption of infrared beam (source) by water vapor and CO_2 at their absorption wavelengths (2.59 and $4.26 \mu\text{m}$ respectively). Detector is a thermo-electrically cooled lead selenide. Data from LI-7500 was collected through RS-232 interface in a PC at the rate of 10 Hz. Accuracy of the instrument for CO_2 is 1% nominal and 1% for H_2O . During rain, flying droplets and flakes in the optical path affect the performance of LI-7500, even if the total light blockage is small. Hence, the spikes due to rain and other adverse effects have been eliminated in the data analysis.

The time synchronized outputs from sonic anemometer (u , v , w and T) and $\text{H}_2\text{O}/\text{CO}_2$ analyzer (CO_2 and water vapor mass densities), were sampled at 10 Hz. Each half hour data set contained 18000 samples, which was used to compute half hour averages of total horizontal wind speed (U), Monin – Obukhov stability parameter (ζ) and

CO₂ - water vapor correlation coefficient (γ). The standard error for u , v , w , T , CO₂, H₂O and their co variances were computed and used to determine the confidence level (CL). The equations used for the computation of U , ζ , fluxes and correlation coefficient are as follows,

$$U = \sum_{i=1}^N \sqrt{u_i^2 + v_i^2} \quad (1)$$

Where N is the number of samples.

$$\zeta = \frac{z}{L} = - \frac{kz g (\overline{w' T_v'})_s}{\overline{T_v} u_*^3} \quad (2)$$

where k is the von Karman constant, z the height of measurement (5m),

$$\overline{w' T_v'} = \frac{1}{N} \sum_{i=1}^N (w_i - \overline{w})(T_{vi} - \overline{T_v}) \quad (2a)$$

$\overline{T_v}$ the half hour averaged virtual temperature obtained from sonic anemometer and

$$u_* \text{ is the friction velocity} = \left[\overline{u' w_s'^2} + \overline{v' w_s'^2} \right]^{\frac{1}{4}} \quad (2b)$$

$$\gamma_{qCO_2} = \frac{\overline{q' CO_2}}{\sigma_{CO_2} \sigma_q} \quad (3)$$

Where q' is the fluctuation in mass density of water vapor and O_2 that for CO₂. σ_C is the standard deviation of CO₂ and σ_q for water vapor.

The CO₂, water vapor, temperature (T_v), wind speed (u , v and w component) and wind direction were measured at the Vasco-da-Gama station. We estimated the Monin-Obukhov (M-O) length (L) by eddy correlation method using equation (1) to establish the stability regime. To look into the relation of stability with CO₂ and water vapor, the entire dataset for four months (July–October) was separated into unstable and stable cases based on non-dimensional M-O length scale (z/L).

z being the observational height and L the Monin-Obukhov length. $w'\theta'$ is the surface sensible heat flux and u_* is the frictional velocity. Where the primes represent the fluctuations and over bars, the averages over the period are long enough to assure stationarity. The u , v and w are the longitudinal, lateral and vertical components of wind, respectively. Positive magnitude of z/L indicates stable conditions and vice versa.

In the west coast station Vasco-da-Gama, the wind reaching the site depending on its direction can bring two types of air masses from land or sea with entirely different characteristics. To capture every nuance of the air masses, we studied the geometry of the site and came to the conclusion that the wind approaching the coast from 0° to 135° is from land and the rest (135° - 360°) from the sea. Even though the winds encompassing 0° to 90° is considered to be mostly from land such winds have to

pass through back waters before reaching the site. For this reason it is suspected that there will be mixing of marine air with the land originated air mass. Similarly, the SE-S (135° - 180°) and NW-N (315° - 360°) sector wind travels mostly over sea, including a small portion of land. Hence, only the winds from E-SE sector (90° - 135°) and that from S-NW (180° - 315°) are exclusively from land and sea, respectively. We considered only those half hour data sets that have at least 75% of the wind clearly from land or sea.

RESULTS AND DISCUSSION

Diurnal variation of wind speed, stability, correlation of CO₂ and water vapor

Figure 2a-d shows the diurnal variation of wind speed, over the west coastal station Vasco-da-Gama, for the months during July to October 2002, respectively. Winds in general were mostly from sea during July and August, due to large scale south west monsoon winds prevailing over the region (Cini et al., 2005). In July 2002 light to moderate winds of speed 2 – 6 ms⁻¹ prevail mostly in early morning and night hours. Occasionally wind speed increased and reached a maximum (> 7 ms⁻¹) by evening (1600 – 2000 hrs IST). Winds in August too were light to moderate during early morning hours (~ 0400 hrs IST) and in the evening $U = 1-7.5$ ms⁻¹. Wind speed in September showed normal skew symmetric distribution with a minimum (~ 1 ms⁻¹) during 0000 – 0400 hrs IST and maximum in the afternoon (1500 – 1600 hrs IST). Less data points in early morning hours of September and gaps shown in data in October are due to winds from land. Maximum wind speeds were 6 ms⁻¹ between 1200 and 1600 hrs IST in the month of October over Vasco-da-Gama. Figure 2e shows the winds from land in the months of September and October (combined). Winds were light (< 2 ms⁻¹) during 0200 to 1000 hrs IST at the experimental station.

Figure 3a-d shows the time series of z/L and γ for July, August, September and October 2002 over Goa. Stability parameter z/L indicates (Figure 3a) that the atmosphere was stable in the early morning up to 0800 hrs IST and in the night (2000 – 2400 hrs IST). Stability was strong ($z/L \sim 0.18$) around 0430 hrs IST. Instability prevailed during noon and afternoon hours with $-0.05 < z/L < 0$ around 1200 – 1300 hrs IST. The gradual transition from stable to unstable and vice versa in the forenoon and evening hours with neutral atmosphere in between is very clear. The stability parameter reveals a clear sinusoidal oscillation of period about 1 day in July 2002. Diurnal variation of γ (Figure 3b) showed in phase variation with that of stability during the day (0800 – 1700 hrs IST). Fluctuation of γ is positive and negative, during morning (0000 – 0800 hrs IST), evening and night (1700 – 2400 hrs IST) hours. Irrespective of the sign, correlation coefficient

Temporal variation of carbon dioxide and water vapor density over a station in west coast of Arabian Sea during sea breeze and land breeze

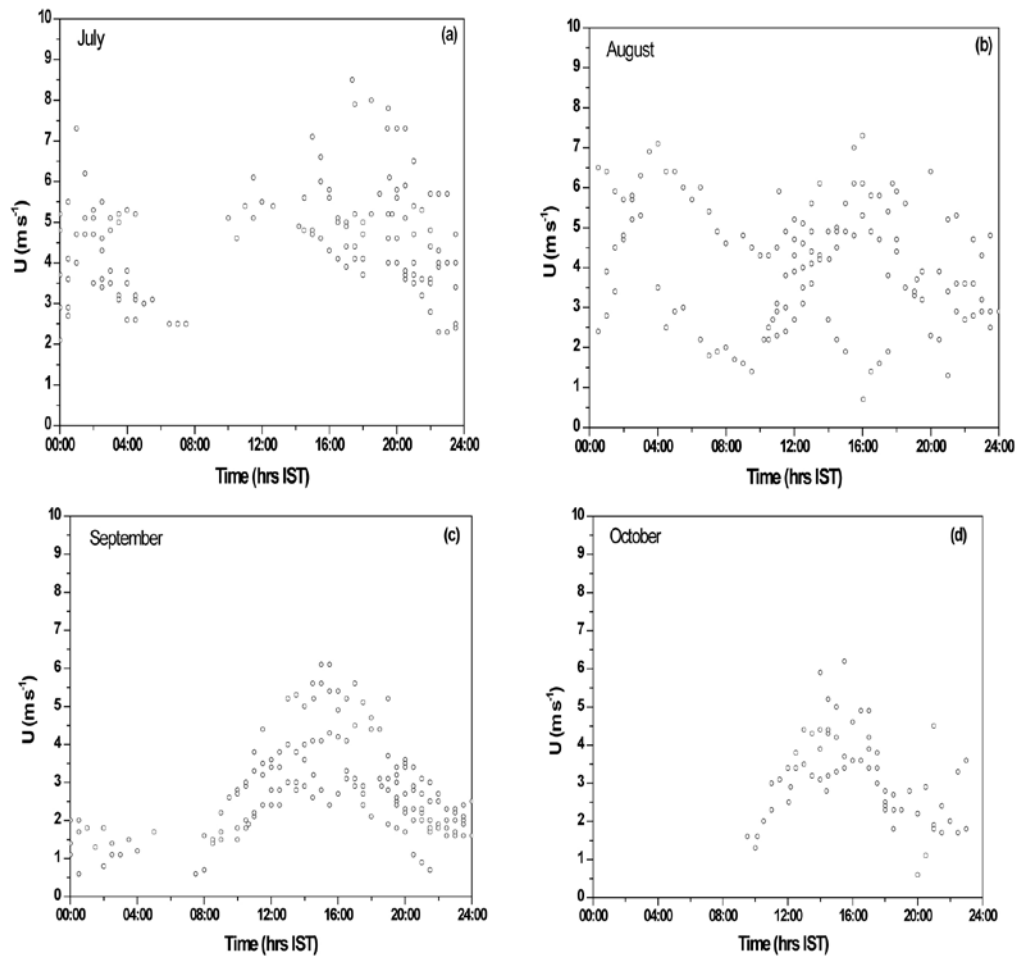


Figure 2. Diurnal variation of horizontal wind speed (U) in July (a), August (b), September (c) and October (d) in the year 2002 when the winds are from sea.

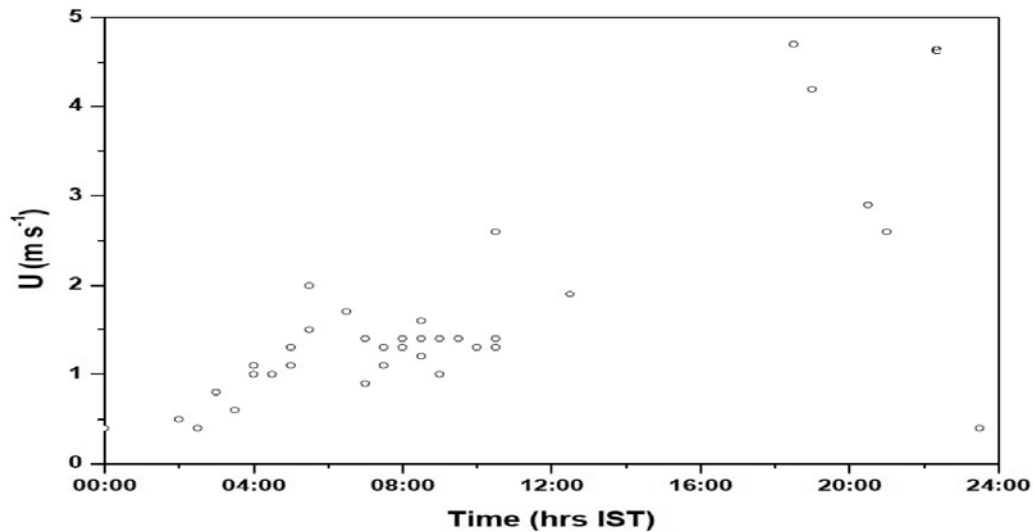


Figure 2e. Diurnal variation of horizontal wind speed (U) in September and October (combined) in the year 2002 when winds are from land.

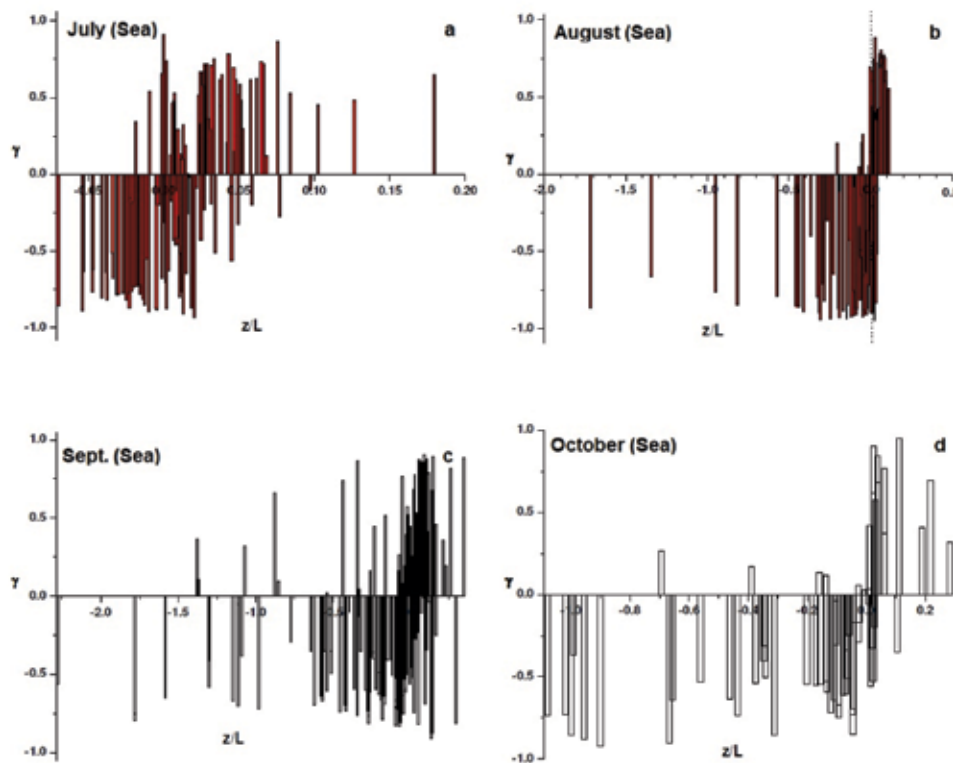


Figure 3. Relation between stability (z/L) and γ for the months of July (a), August (b), September (c) and October (d) in the year 2002 over Goa when the winds are from sea.

was significant ≥ 0.5 in most of the cases. Variation of γ with stability parameter is brought out well in Figure 3c. During unstable condition γ is negative and positive during stable condition (> 0.5). Near neutral conditions ($-0.02 < z/L < 0.06$) γ is positive or negative.

It is seen that the atmosphere is stable to near neutral in early morning and night Figure 3a, whereas during day time between 0800 and 1800 hrs IST, it is unstable. Instability is very strong during 1000-1130 hrs IST, showing that convective activity has begun. Prevailing high wind speed between 0000 hrs IST and 0600 hrs IST and moderate winds between 2000 hrs IST and 2400 hrs IST gives rise to mixing of air mass, which resulted in near – neutral stability.

Significant values of γ ($\sim \pm 0.7$) and changing sign frequently during 0000 – 0800 hrs IST and 2000 – 2400 hrs IST show presence of stable to near neutral transition phase (Figure 3b and c). During noon and afternoon hours γ showed negative values with magnitudes tending to perfect correlation (≥ 0.95). Figure 3c clearly shows that when the atmosphere is unstable (stable), negative (positive) correlation persists. For near – neutral conditions, γ is either positive (stable side) or negative (unstable side).

Figure 4a-d shows the time series of mean wind speed (U) and γ for July, August, September and October 2002 over Goa, respectively. When the winds are from the Arabian

Sea the variation of CO_2 and water vapor correlation coefficient (γ) as a function of the stability parameter (z/L) and wind speed is noticed, as shown in Figures 4c and d. Figure 4d distinctly shows the effect of U on γ . At low wind speeds ($< 4 \text{ m s}^{-1}$) γ is mostly positive, whereas it becomes negative during moderate ($4 - 6 \text{ m s}^{-1}$) and high wind speeds ($> 6 \text{ m s}^{-1}$). It is evident that in July 2002 negative correlation is significant at moderate and high wind speeds and positive correlation at light/low winds. In the figure 4d variation of γ with U shows both positive and negative correlations at high, low and moderate wind speeds. In light winds $< 3 \text{ m s}^{-1}$, when free convection is prevailing, high negative correlation indicates possible absorption of CO_2 by water vapor. Dharmaraj et al., (2012) reported that the magnitude of mean CO_2 for the monsoon season was $545-650 \text{ mg m}^{-3}$. This is comparable to the value reported for some coastal stations in Europe (Sirignano et al., (2010). They have also shown that for the time scale $< 1 \text{ hr}$, an inverse relationship of CO_2 with water vapor is observed.

Figure 5a-d depicts the variation of the parameters in the months of July, August, September and October 2002, over Goa. In Figure 5a, time series of z/L has close resemblance to that of August 2002 (figure 5c). Near neutral atmosphere in the early morning and night hours and high instability

Temporal variation of carbon dioxide and water vapor density over a station in west coast of Arabian Sea during sea breeze and land breeze

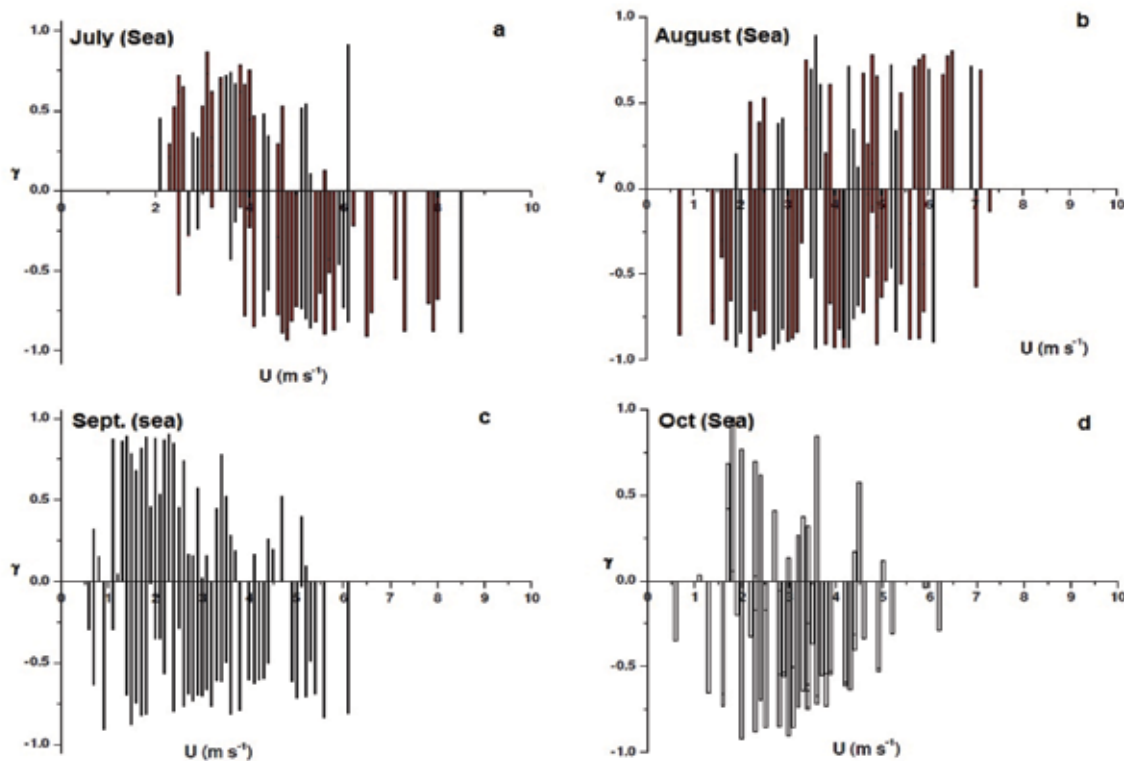


Figure 4. Relation between wind speed and γ for the months of July (a), August (b), September (c) and October (d) in the year 2002 over Goa.

($z/L > -1$) in day time is evident. Variation in γ is mostly negative (Figure 5b) when the atmosphere is unstable between 1000 hrs IST and 1800 hrs IST. As in July and August, γ values fluctuate between positive and negative when the atmosphere is near neutral. In Figure 5b and c except the positive correlations that occurred around 0800 – 0900 hrs IST, negative γ dominated during unstable atmospheric conditions. Clustering of points during near neutral conditions is revealed in Figure 5c.

Positive and negative correlations (Figure 5d) occurred equally for low wind speeds. There is a tendency for γ to become negative during moderate ($4 - 6 \text{ ms}^{-1}$) to high winds. Contini et al., (2012) reported that the upward CO_2 fluxes dominate completely over deposition and the area behaved as a source of aerosol. Also they have shown that the measured CO_2 flux/traffic rate showed a limited correlation with friction velocity and stability, because of the influence of the biogenic cycle, thereby micrometeorological parameters were not used in the parameterization of CO_2 flux.

Figure 6a-d is similar to the Figure 5. In the month of October 2002 the winds blow from sea as in July and August, but they are not associated with south west monsoon. $\text{H}_2\text{O} - \text{CO}_2$ correlations (Figure 6b) show both negative and positive values at night (2000 – 2400 hrs IST). When instability prevails (Figure 6a and c) they

reflect variations similar to that in September. Correlation during 0930 – 1600 hrs IST is negative during unstable conditions but positive and negative in near neutral conditions. Variation of γ with U closely resembles that in September. In low wind speed γ shows both signs but more negative correlations in September (Figure 5d).

Figure 7a-b represents those cases in the months of September and October combined, when winds are from land. Atmosphere is stable during 0230 – 0430 hrs IST (Figure 7a) and becomes unstable from 0700 – 1030 hrs IST. Around 1030 hrs IST instability sets in under the influence of sea breeze, as seen in Figure 7a. During unstable conditions γ is mostly negative and becomes positive in stable conditions (Figure 7b). In Figure 7b γ fluctuated between positive and negative in low wind speeds ($U < 2 \text{ ms}^{-1}$).

Brummer et al., (2008) reported from eddy co-variance (EC) measurements of carbon dioxide and energy exchange in a savanna in sub-Saharan, West Africa that during the transition months between dry and wet season (April–June) as well as between wet and dry season (October) the ecosystem atmosphere CO_2 flux responded immediately to changes in water availability.

Figures 2–7 reveal clearly during unstable conditions the existence of inverse relationship between CO_2 and water vapor densities at this coastal site, which is

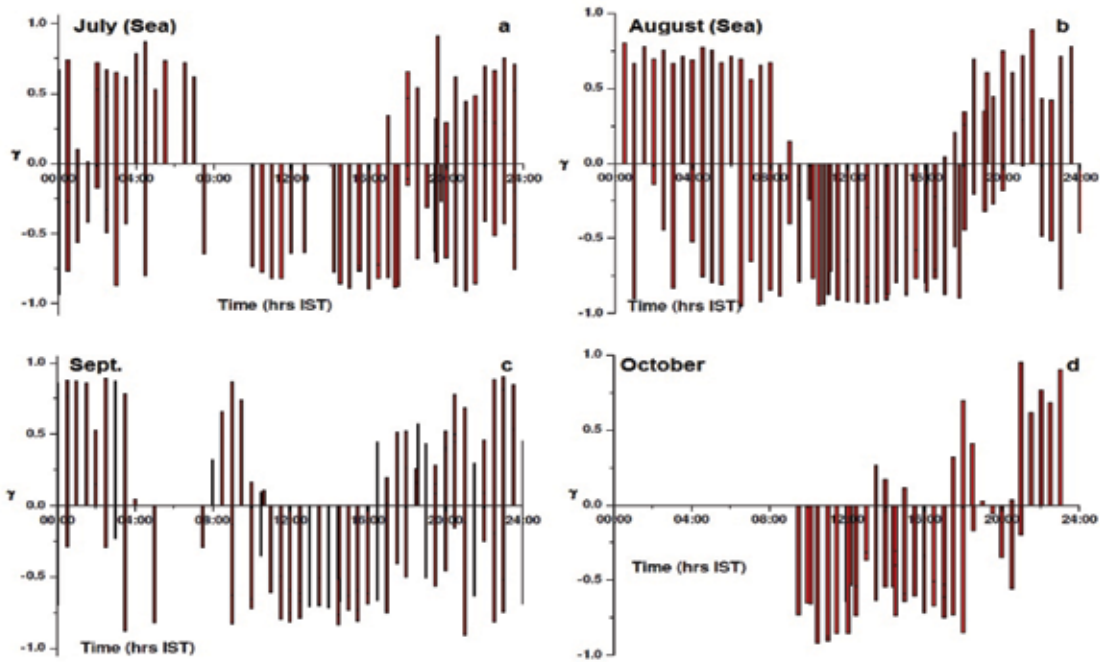


Figure 5. Variation of γ for the months of July (a), August (b), September (c) and October (d) in the year 2002 over Goa when the winds are from sea.

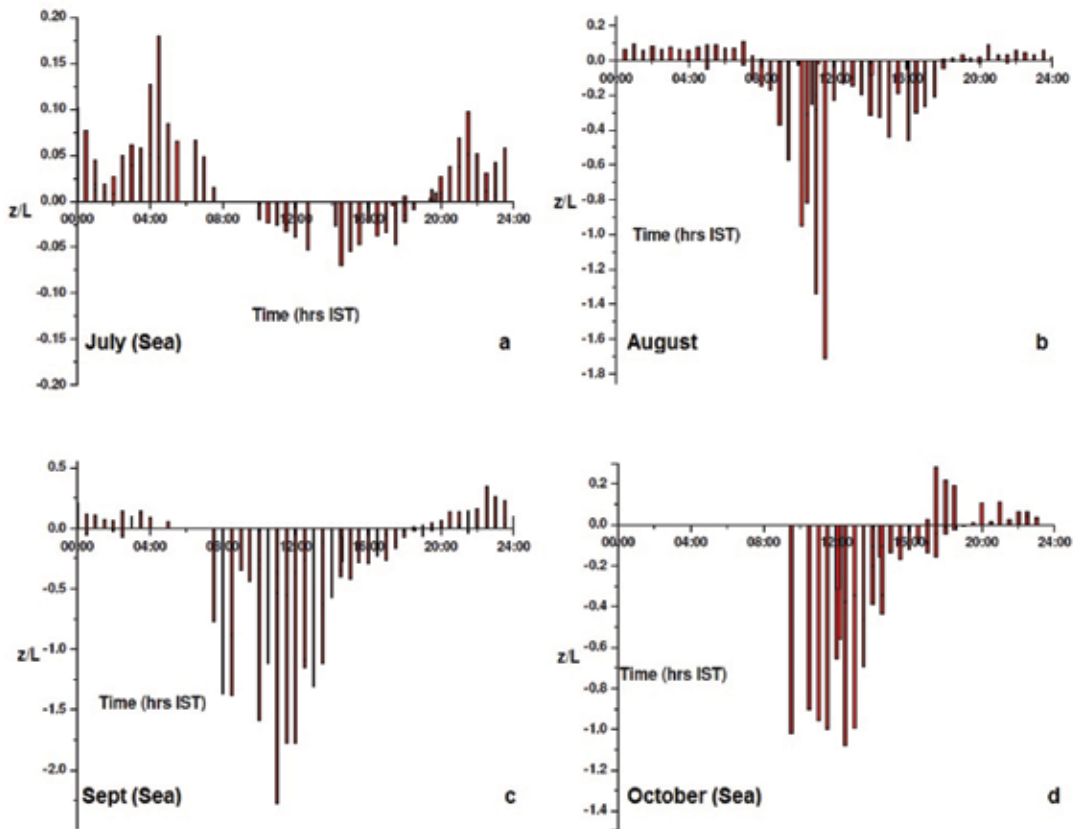


Figure 6. Variation of stability for the months of July (a), August (b), September (c) and October (d) in the year 2002 over Goa when the winds are from sea.

Temporal variation of carbon dioxide and water vapor density over a station in west coast of Arabian Sea during sea breeze and land breeze

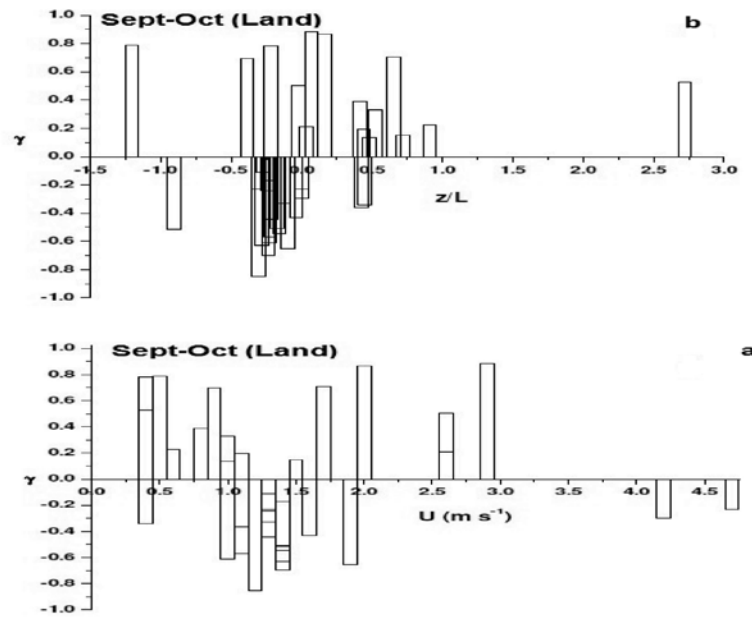


Figure 7. Relation between stability (z/L) and γ for the months of September and October 2002 during wind from land over Goa.

similar to that observed over a vegetative canopy. During photosynthesis CO_2 is absorbed by vegetation and water vapor diffuses into the atmosphere simultaneously through leaf stomata. Measurements at the site in Goa are influenced by surrounding vegetation and also the advection of marine air mass due to sea breeze. Sea surface waters with large chlorophyll content (Prasanna Kumar et al., 2000; Bhattathiri et al., 1996) in the Arabian Sea help phytoplankton to multiply and their transpiration results in CO_2 fluctuation during advection of marine air mass. There is a sufficient amount of vegetation surrounding the tower during the monsoon season which is also responsible for CO_2 and water vapor fluctuations. Thus, the negative (positive) correlation for unstable/day time (stable/ night time) conditions could be attributed to vegetation/phytoplankton activity. In near saturation (water vapor density ~ 23 to 25 gm^{-3}) conditions, there is a possibility for CO_2 absorption in water vapor/ droplets, thus CO_2 decreases when water vapor increases. During night time, fall in air temperature gives rise to decrease in both the content of water vapor in air (due to decrease in water holding capacity of air) and CO_2 absorption. CO_2 absorption by phytoplankton also stops but its release by respiration exists. The two effects probably combine to give positive correlations during night time stable atmosphere. During neutral and near neutral cases the correlation is positive and negative.

Figure 8a-d depicts the diurnal variation obtained by averaging the half hourly observations of CO_2 and water vapor for the case when winds are from sea/land in July, August, September and October 2002 respectively.

In July the inverse relationship between CO_2 and water vapor is less prominent in all the hours except 1600 – 2330 hrs IST. In August inverse relationship is not well depicted but mixed ones are seen between 0800 hrs IST and 1230 hrs IST and also between 1600 hrs IST and 2000 hrs IST. There are cases of land breeze in the early morning and forenoon hours, apart from the winds from sea in September. The inverse relationship is found to get masked during 0000 to 1200 hrs IST, whereas after 1200 to 2330 hrs IST a very clear inverse relationship is depicted. In the month of October also a fairly good inverse relationship is seen after 1200 hrs IST, when sea breeze sets in.

The obscurity in inverse relationship in monsoon months (July and August) can be due to the effect of predominant large scale monsoon circulation on local features such as sea and land breezes. In Figure 8c between 0000 – 1200 hrs IST Sea and land breezes occur during withdrawal phase of monsoon and the time of onset of sea breeze is around noon. So, by averaging the CO_2 and water vapor mass densities of few days for a particular hour has shown that the inverse relationship existed during day time after the onset of sea breeze.

Daily variation of CO_2 and water vapor over Goa

Figure 9 shows the daily mean variation of CO_2 and water vapor for the period July to October 2002. A significant number (48 per day) of available half hour averages have been used to compute the daily mean. During that period quantum of CO_2 varied between $585\text{--}650 \text{ mg m}^{-3}$, while the water vapor density varied between $18\text{--}27.5 \text{ g m}^{-3}$.

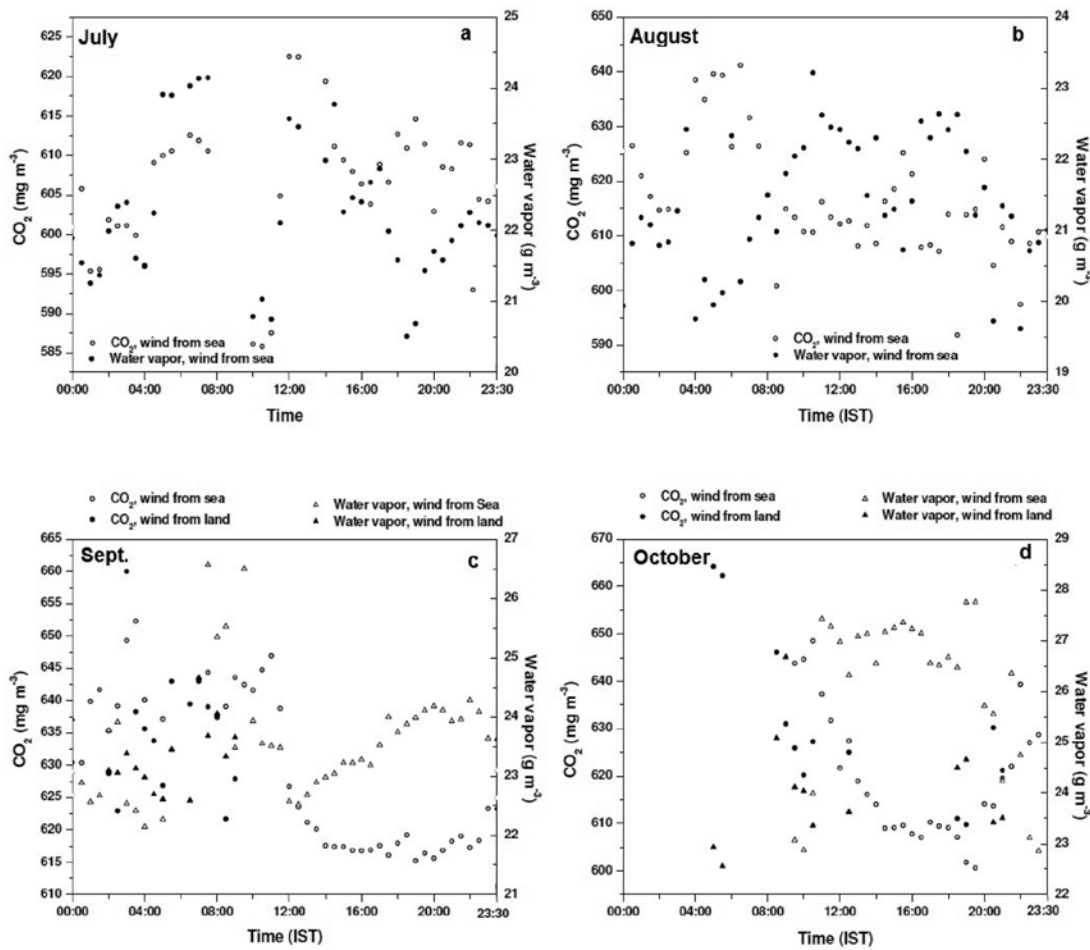


Figure 8. Diurnal variation of half hourly averaged CO₂ and water vapor for July (a), August (b), September (c) and October (d) in the year 2002 over Goa.

Measurements of CO₂ carried out elsewhere over different stations at various latitudes and longitudes show that the mean annual value for the year 2002 is 666 mg m⁻³ (Denning, et al., 1996a,b, 1995, <http://cdiac.esd.ornl.gov>). In day to day variation (Figure 9) inverse relationship is not clear because all the stable, unstable and neutral cases have been clubbed in the daily mean. This shows that the inverse relationship depends on wind speed, atmospheric stability, sea breeze onset and phytoplankton activity, which belong to micro and meso scale phenomena.

For better understanding of the inverse relationship between CO₂ and water vapor mass densities, we averaged separately the half hour samples corresponding to stable and unstable hours of each day for all the four months successively (Figure 10). We obtained in all about 29/26 days when stable/unstable conditions prevailed during the period (July 8/6, August 7/6, September 11/8 and October 3/6) of which 99/39, 53/77, 73/110 and 19/45 half hour samples showed stable/unstable atmospheric conditions in the surface layer in July to October 2002, respectively. Figure 10a shows the CO₂ - water vapor and wind speed

variation as a progression in time for unstable case. Figure 10b shows for stable case. We observe the existence of inverse relationship in most of the cases. Wind speed during the period shows moderate to high winds in July and August, whereas it is light during unstable conditions in August and calm to very light in stable conditions.

In October winds are light/moderate during stable/unstable conditions. The effect of wind speed on CO₂ and water vapor can be seen in Figure 10. During unstable conditions a steep increase/decrease in wind speed result in a steep decrease/increase in CO₂. This could be due to CO₂ absorption by water vapor at moderate winds. The Monin – Obukhov (M-O) stability parameter (z/L) and the correlation coefficient (γ) for CO₂ and H₂O was computed from turbulent fluctuations of the measured parameters. Variation of γ with z/L has been found to be negative in unstable conditions and positive in stable condition.

Air–sea interactions and ocean circulations determine the magnitude of CO₂ in the marine atmosphere, which in turn controls the coastal atmospheric CO₂ through advection of marine air mass. However, there are few

Temporal variation of carbon dioxide and water vapor density over a station in west coast of Arabian Sea during sea breeze and land breeze

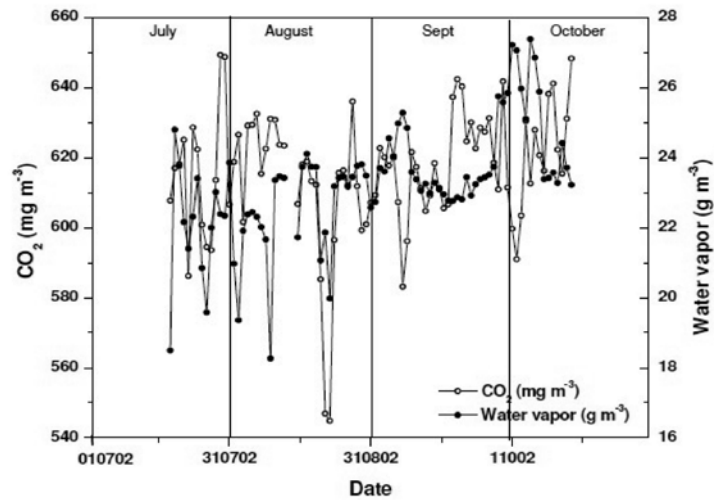


Figure 9. Daily averages of CO₂ and water vapor over Goa during the period from July to October in the year 2002.

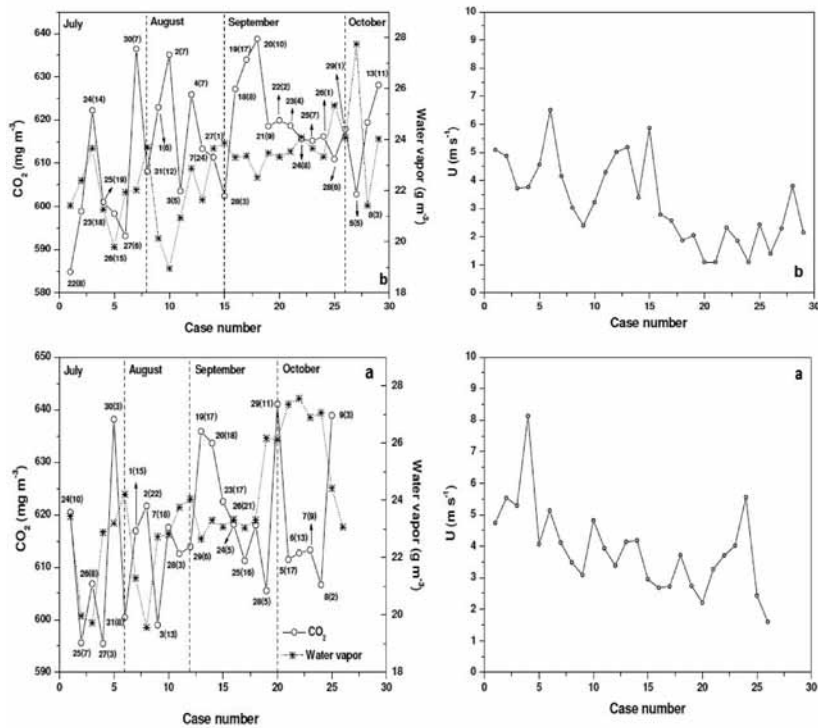


Figure 10. Mean variation of CO₂, water vapor and wind speeds (*U*) under unstable (a) and stable (b) conditions during the period from July to October in the year 2002.

reports of CO₂ observations over the Indian sub-continent (Patil et al., 2014; Mahesh et al., 2015; Guha and Ghosh, 2014), especially over the west coast, which is influenced by the dynamics of the Arabian Sea in response to the SW (South West) and the NE (North East) monsoons (Latha and Murthy, 2012).

The observation from urban station suggests that the ground-based air-CO₂ is largely affected by the seasonal variability in atmospheric boundary layer condition (Guha and Ghosh, 2014). Seasonal pattern in diurnal variability of mixing ratio and $\delta^{13}\text{C}$ of air-CO₂ was observed at an urban station Bangalore, India (Guha and Ghosh, 2014).

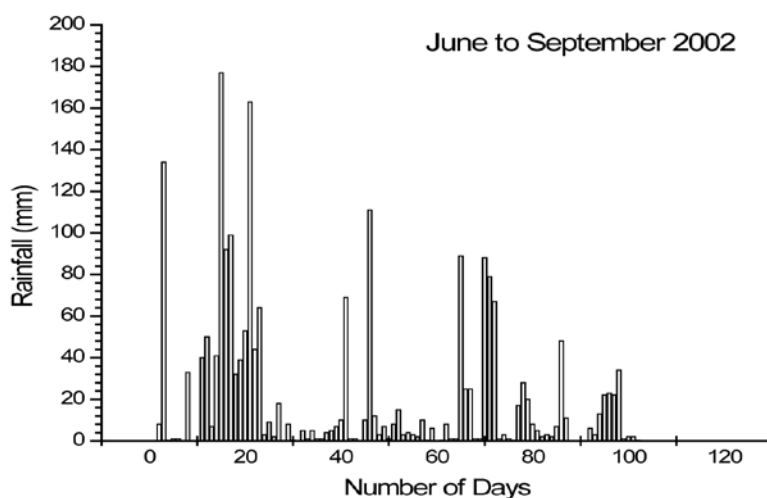


Figure 11. Rainfall distribution over Panjim (Goa) during the period from June to September in the year 2002 reported by IMD.

Impact of land and sea breezes

To study how land and sea breezes affect the CO₂ mixing ratios, we considered all the winds coming from 00-1800 as sea breezes and those coming from 1800-3600 as land breezes. Accordingly CO₂ mixing ratios are divided. Higher concentrations of CO₂ are present during land breeze time. About 70% of the winds are from the Sea. Though coastal regions act as a source of CO₂, the amount of CO₂ concentrations from the ocean are less than those from land (Sarma et al., 2012). Thus, the sea breeze helps in reducing the CO₂ concentrations at Goa. Since sea breeze is stronger than land breeze, the scavenging effect of strong winds is another cause for the low concentrations during sea breeze time.

Impact of rainfall

To understand why the rainfall during October is significantly less during sea breeze, contrary to the other three months during Indian summer monsoon, we analyzed the hourly rainfall data since rainfall is another factor that scavenges the CO₂. Depending upon the partial pressure of CO₂ and the air temperature, CO₂ dissolves in rain droplets producing a weak carbonic acid, H₂CO₃. The daily rainfall during the day (night) time during the period from June to September 2002 is shown in the figure 11.

It is evident that June rainfall was maximum as compared to July, August and September 2002. The comparatively heavy rainfall in October during daytime might have scavenged CO₂ (figure not shown) thus, reducing its relationship with wind speed during sea breeze. Hence, wind speed could explain only 16% of the variations in CO₂ during sea breeze in October.

CONCLUSION

Study of the variation of CO₂ and water vapor in the surface layer (5m AGL) at Goa during the Indian summer monsoon shows that:

An inverse relation in the variation of CO₂ and water vapor exists during unstable atmospheric conditions in August, September and October 2002.

The variation of half hourly averaged values of CO₂ and water vapor is out of phase as corroborated by significant negative correlation during unstable conditions and in phase as shown by positive correlation during stable conditions (both significant at 1% level) of the surface Layer.

The time variation obtained by averaging the half hour values corresponding to a given stability class in a day of a month brings out clearly the positive/negative correlation during the season. The correlation is either positive or negative when the atmosphere is near neutral.

The atmospheric stability therefore has an effect on the daily variation of CO₂ and water vapor.

It has been found that the meso-scale sea and land breeze circulation significantly affects the temporal variation in the mass density of CO₂ and water vapor near the coast.

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Compliance with Ethical Standards:

The authors declare that they have no conflict of interest and adhere to copy right norms.

REFERENCES

- Berner, R.A., 1999. A new look at the long-term carbon cycle: *GSA Today*, v.9, pp: 1– 6.
- Bhattathiri, P.M.A., Pant, A., Sawant, S., Gauns, M., Matondkar, S.G.P., and Mohanraju, R., 1996. Phytoplankton production and chlorophyll distribution in the eastern and central Arabian Sea in 1994-1995. *Curr. Sci.*, v.79, pp: 857-862.
- Brummer, C., Falk, U., Papen, H., Szarzynski, J., Wassmann, R., and Bruggemann, N., 2008. Diurnal, seasonal, and interannual variation in carbon dioxide and energy exchange in shrub savanna in Burkina Faso (West Africa). *J. Geophys. Res.*, v.113 G02030, doi: 10.1029/2007JG000583.
- Cini Sukumaran., Rajitha Madhu Priya, T., Dharmaraj, T., Murthy, B.S., and Sivaramkrishnan S., 2005. Variation of water vapor and CO₂ at Goa during ARMEX phase-I and II. *Mausam*, v.56, no.1, pp: 213-220.
- Contini, D., Donato, A., Elefante, C., and Grasso, F.M., 2012. Analysis of particles and carbon dioxide concentrations and fluxes in an urban area: Correlation with traffic rate and local micrometeorology. *Atmos. Environ.*, v.46, pp: 25–35.
- CO₂ Research group 2002 Scripps Institute of Oceanography, University of California, U.S.A. website <http://cdiac.esd.ornl.gov>.
- Crawford, T.L., Robert, T., McMillen Tilden., Meyers, P., and Bruce Hicks, B., 1993. Spatial and temporal variability of heat, water vapor, carbon dioxide, and momentum air-sea exchange in a coastal environment. *J. Geophys. Res.*, v.98, no.D7, pp: 12,869-12,880.
- Denning, A.S., Collatz, G.J., Zhang, C., Randal, D.A., Berry, J.A., Sellers, P.J., Colello, G.D., and Dazlich, D.A., 1996a. Simulations of terrestrial carbon metabolism and atmospheric CO₂ in GCM. Part 1: Surface carbon fluxes. *Tellus*, v.48B, pp: 521-542.
- Denning, A.S., Fung, I.Y., and Randall, D.A., 1995. Latitudinal gradients of atmospheric CO₂ due to seasonal exchange with land biota. *Nature*, v.376, pp: 240-243.
- Denning, A.S., Randall, D.A., Collatz, G.J., and Sellers, P.J., 1996b. Simulations of terrestrial carbon metabolism and atmospheric CO₂ in a general circulation model. Part 2: Simulated CO₂ concentration. *Tellus*, v.48B, pp: 543-567.
- Dharmaraj, T., Patil, M.N., Waghmare, R.T., and Raj, P.E., 2012. Carbon dioxide and water vapour characteristics on the west coast of Arabian Sea during Indian summer monsoon. *J. Earth. Sys. Sci.*, v.121, no.4, pp: 903–910.
- Guha, T., and Ghose, P., 2014. Diurnal and seasonal variation of mixing ratio and $\delta^{13}\text{C}$ of air CO₂ observed at an urban station Bangalore, India. *Environ. Sci. And Pollution. Res.*, v. 22, no.3, pp: 1877-1890.
- Grimmond, C.S.B., King, T.S., Cropley, F.D., Nowak, D.J., and Souch, C., 2002. Local-scale fluxes of carbon dioxide in urban environments: methodological challenges and results from Chicago. *Environ. Poll.*, v.116, pp: S243–S254.
- Heimann, M., Keeling, C.D., and Tucker, C., 1989. A three dimensional model of atmospheric CO₂ transport based on observed winds, 3, Seasonal cycle and synoptic time scale variations, in *Aspects of Climate Variability in the Pacific and the Western Americas*. *Geophys. Monogr. Ser.*, v.55, pp: 277-303, AGU, Washington, D.C.
- Jones, E.P., and Smith, S.D., 1977. A first measurement of sea-air CO₂ flux by eddy correlation. *J. Geophys. Res.*, v.82, pp: 5990-5992.
- Jones, E.P., Ward, T.V., and Zwick, H.H., 1978. A fast response atmospheric CO₂ sensor for eddy correlation flux measurements. *Atmos Environ.*, v.12, pp: 845-851.
- Keeling, C.D., Bacastow, R.B., Carter, A.F., Piper, S.C., Whorf, T.P., Heimann, M., Mook, W.G., and Roeloffzen, H., 1989. A three-dimensional model of atmospheric CO₂ transport based on observed winds, 1, Analysis of observational data, in *Aspects of Climate Variability in the Pacific and the Western Americas*. *Geophys. Monogr. Ser.*, v.55, pp: 165–236, AGU, Washington, D. C.
- Latha, R., and Murthy, B.S., 2012. Natural reduction of CO₂ observed in the pre-monsoon period at the coastal station, Goa. *Meteorol. Atmos. Phys.*, v.115, pp: 73-80. DOI: 10-1007/s00703-011-0164-6.
- Louanchi, F., Metzl, N., and Poisson, A., 1996. A modelling the monthly sea surface fCO₂ fields in the Indian Ocean. *Mar. Chem.*, v.55, pp: 265-280.
- Leuning, R., Denmead, D.T., Lang, A.R.G., and Ohtaki, E., 1982. Effects of heat and water vapor transport on eddy covariance Measurement of CO₂ fluxes. *Bound. Layer. Meteorol.*, v.23, pp: 209-222.
- Mahesh, P., Sreenivas, G., Rao, P.V.N., Sai Krishna, S.V.S., and Mallikarjun, K., 2015. High-precision surface-level CO₂ and CH₄ using off-axis integrated cavity output spectroscopy (OA-ICOS) over Shadnagar, India. *International. J. Remote. Sens.*, v.36, no.22, pp: 5754-5765.
- Mook, W.G., 1986. $\delta^{13}\text{C}$ in atmospheric CO₂. *Ned. J. Sea. Research.*, v.20, pp: 211–223.
- Monastersky, R., 2013. Global carbon dioxide levels near worrisome milestone. *Nature*, v. 497, no.7447, pp: 13-14.
- Ohtaki, E., 1985. On the similarity in Atmospheric fluctuations of CO₂, water vapor and temperature over vegetated fields. *Bound. Layer. Meteorol.*, v.32, pp: 25-37.
- Ohtaki, E., and Matsui, M., 1982. Infra Red Device for simultaneous measurements of Atmospheric CO₂ and water vapor. *Bound. Layer. Meteorol.*, v.24, pp: 109-119.
- Patil, M.N., Dharmaraj, T., Waghmare, R.T., Prabha, T.V., and Kulkarni, J.R., 2014. Measurements of carbon dioxide and heat fluxes during monsoon-2011 season over rural site of India by eddy covariance technique. *J. Earth. Sys. Sci.*, v.123, pp: 177-185.

- Prasanna Kumar, S., Madhupratap, M., Dilip Kumar, M., Gauns, M., Muraleedharan, P.M., Sarma, V.V.S.S., and De Souza, S.N., 2000. Physical control of primary productivity on a seasonal scale in Central and Eastern Arabian Sea. *Proc. Indian. Acad. Sci. (Earth Planet Sci)*, v. 109, no4, pp: 433-441.
- Sarma, V.V.S.S., Kumar, M.D., George, M.D., and Rajendran., 1998. The central and eastern Arabian Sea as a perennial source of atmospheric carbon dioxide. *Tellus.*, v.50B, no.2, pp: 179-184.
- Sivaramakrishnan, S., Murthy, B.S., Dharmaraj, T., Cini Sukumaran., and Rajitha Madhu Priya, T., 2003. Measurement of Profiles and Surface Energy Fluxes On the west Coast of India at Vasco-Da-Gama, Goa During ARMEX 2002-03. IITM Research Report, v. RR-099; IITM, SSN 0252-1075.
- Sarma, V.S., Krishna, M.S., Rao, V.D., Viswanadham, R., and Kumar, N.A., 2012. Sources and sinks of CO₂ in the west coast of Bay of Bengal. *Tellus. Series B Chem. Phy. Meteor.*, v.64, pp: 1-10.
- Sharma, N., Dadhwal, V.K., Kant, Y., Mahesh, P., and Mallikarjun, K., 2014. Atmospheric CO₂ Variations in Two Contrasting Environmental Sites Over India. *Air, Soil Water Res.*, v.7, pp: 61-68.
- Sharma, N., Nayak, R.K., Dadhwal, V.K., Kant, Y., and Ali, M.M., 2013. Temporal variations of atmospheric CO₂ in Dehradun, India during 2009. *Air Soil Water Res.*, v. 6, pp: 37-45.
- Sirignano, C., Neubert, R.E.M., C. Rödenbeck, C., and Meijer, H, A.J., 2010. Atmospheric oxygen and carbon dioxide observations from two European coastal stations 2000–2005: Continental influence, trend changes and APO climatology. *Atmos. Chem. Phys.*, v.10, pp: 1599–1615.
- Takahashi, T., 1989. The carbon dioxide puzzle. *Oceanus.*, v.32, pp: 22-29.
- Tans, P.P., Fung, I.Y., and Takahashi, T., 1990. Observational constraints on the global atmospheric CO₂ budget. *Science.*, v.247, pp: 1431-1438.
- Velasco, E., and Roth, M., 2010. Cities as Net Sources of CO₂: Review of Atmospheric CO₂ Exchange in Urban Environments Measured by Eddy Covariance Technique. *Geography Compass.*, v.4/9, pp: 1238–1259.
- Watson, A.J., Robinson, C., Robinson, J.E., Williams, P.J.L.B., and Fasham, M.J.R., 1991. Spatial variability in the sink for atmospheric carbon dioxide in the North Atlantic. *Nature.*, v.350, pp: 50-53. doi:10.1038/350050a0.

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Quotations on Carbon Dioxide

* “Plate tectonics is not all havoc and destruction. The slow movement of continents and ocean floors recycles carbon dioxide dissolved in the oceans back into the atmosphere. Without this slow speed carbon cycle, Earth’s temperatures would cool dozens of degrees below your comfort zone”.

-*Seth Shostak (1943--)* is an American astronomer, currently Senior Astronomer for the SETI Institute

* “Organisms in the ocean provide over 40 percent of the oxygen we breathe, and they’re the major sink for capturing all the carbon dioxide we constantly release into the atmosphere”.

-*Craig Venter (1946--)* is an American biotechnologist, biochemist, geneticist, and businessman.

* “We can look back through ice-core data and see over 800,000 years, relationships between carbon dioxide and the temperature of the world. So those people who deny the importance of climate change are just wasting their time. They’re also being diversionary because if we don’t act the risks are enormous”.

-*Nicholas Stern (1946--)* is a British Economist.

* “Healthy forests and wetlands stand sentry against the dangers of climate change, absorbing carbon dioxide from the atmosphere and locking it away in plants, root systems and soil”.

-*Frances Beinecke (1949--)* is the former president of the Natural Resources Defense Council

* “We’re running the most dangerous experiment in history right now, which is to see how much carbon dioxide the atmosphere... can handle before there is an environmental catastrophe”.

-*Elon Musk (1971--)* is a South African born Canadian American business magnet, investor and engineer.