

## Intertidal zones as carbon dioxide sources to coastal oceans

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To understand the factors controlling carbon dioxide ( $\text{CO}_2$ ) exchanges near land-sea boundary diurnal observations have been made twice on  $\text{CO}_2$  in the air and water in a coastal region. The results suggest that  $\text{CO}_2$  enrichment in intertidal water, relative to that in the nearshore water, is directly proportional to  $\text{CO}_2$  abundance in air and it provides evidence for the supply of  $\text{CO}_2$  from intertidal zone to nearshore region with tidal currents.

Coastal oceans are significant in mediating climatic change as these are the zones first to absorb anthropogenic  $\text{CO}_2$ . Studies on carbon exchange near continental boundaries are being aimed to understand the influence of these margins on ocean chemistry and climate<sup>1</sup>. The absorption shall be more pronounced for  $\text{CO}_2$  in the intertidal zones compared to open coastal systems since the former are more turbulent. Despite their significance in material transfer in global reservoir network i.e. air-sea-land) these regions remain unattended to. In this paper the dynamics of  $\text{CO}_2$  in a coastal region through its variations in air and water, is reported.

### Materials and Methods

Two 24 h observations, with 3 hourly sampling interval, were made on total carbon dioxide ( $\text{TCO}_2$ ) in water of intertidal (ITZ) and nearshore zones (NSZ) and in air at a station ( $15^\circ 25' \text{N}$ ,  $73^\circ 45' \text{E}$ ) in Goa (central west coast of India). Observations were made from 0530 hrs on 6th (Expt. I) and from 0830 hrs on 13th (Expt. II) October 1990. Air was vacuum sampled at 20 m height from the ground which is 200 m away from the ITZ sampling point. Having sampled the air into one litre glass flasks, after 10 min of continuous flushing, samples were sealed and brought to the laboratory. Carbon dioxide was measured by a carbon coulometer (UIC Inc, USA). Analyses were done in duplicate and the error was found to be within  $\pm 5$  ppmv (a precision of 1.43%). Wind velocity ( $\text{km.h}^{-1}$ ) and directions were obtained from an observatory (India Meteorology Department, Panaji) that is 5 km away from the field site. NSZ water was not filtered while ITZ water was filtered, *in situ*, using a Milli-

pore in-line filter holder with  $0.40 \mu\text{m}$  Nucleopore filter fitted to a glass syringe. Bottom and pore water were collected from ITZ by keeping the tip of the filter holder close to the sediment-water interface and by inserting the tip 1 cm deep in to sediments, respectively. Samples were transferred to the laboratory in 60 ml stoppered glass bottles with no air space inside and  $\text{CO}_2$  was analysed immediately coulometrically<sup>2</sup>. An aliquot of the sample (25 ml) was acidified with 5 ml of 4N  $\text{HClO}_4$  and the  $\text{CO}_2$  was purged out by  $\text{CO}_2$  free air. High purity calcium carbonate standards were used for calibration. Analysis of replicates yielded a precision of better than  $\pm 0.15\%$ .

### Results and Discussion

Atmospheric  $\text{CO}_2$  was  $< 335$  ppmv between 0830 and 2030 hrs but was greater, to a maximum of 401 ppmv during the rest of the time (Fig. 1A). These concentrations agree with observations made elsewhere<sup>3</sup> (and references therein) except for high values obtained towards the end of both experiments. Carbon dioxide in air at the land-sea boundary reflected its sources: marine air being the source during day time whereas it was air from land at night, especially in the early hours. Low  $\text{CO}_2$  during the day time was due to  $\text{CO}_2$  fixation when organic matter was synthesized and at night, higher amounts were predominantly due to respiration. Very high atmospheric  $\text{CO}_2$  in the morning hours of 7th and 14th October were due to respired  $\text{CO}_2$  along with some anthropogenic component, as the wind continued to blow from land to sea. During Expt. I wind mostly blew from sea to land and transported a net landward  $\text{CO}_2$  flux of  $53 \text{ kg CO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  that came down to  $3 \text{ kg CO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  in the same direction

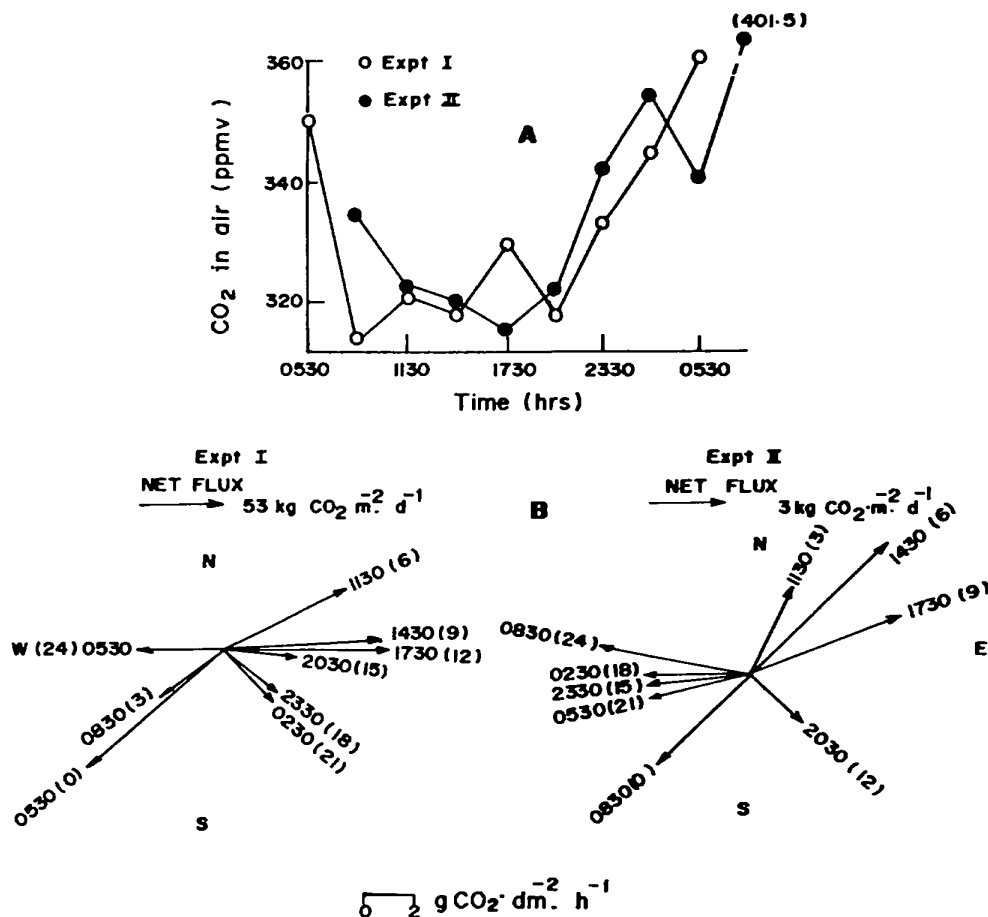


Fig. 1-(A) Temporal variability in atmospheric carbon dioxide during 6-7 October 1990 (Expt. I) and 13-14 October 1990 (Expt. II), (B) atmospheric carbon dioxide fluxes during Expts I and II. [Numbers indicate the time of observation while those in brackets refer to the duration from the beginning of the experiment. Note that the Arabian Sea is to the west of the sampling site]

during Expt. II because of the varied wind pattern (Fig. 1B). Here the flux was calculated as a product of CO<sub>2</sub> in air (kg. m<sup>-3</sup>) and the wind speed. The wind speeds observed were between 4 and 12 km.h<sup>-1</sup>. The net flux is the difference between the total CO<sub>2</sub> fluxes transported by sea and land air. Maxima in wind velocities occurred between 1000 and 1900 hrs in general and hence Fig. 1B depicts the resultant large amounts of CO<sub>2</sub> fluxes from sea to land during that time.

Nearshore zone water contained less TCO<sub>2</sub> than that by the ITZ water (Fig. 2). The CO<sub>2</sub> enrichment in ITZ water is more pronounced at low tide. TCO<sub>2</sub> in pore water of ITZ is higher than that in the overlying water, except at 2030 hrs (Fig. 2B). Pore water TCO<sub>2</sub> was also very high

during low tides, which could be due to bacterial activity in intertidal sediments<sup>4</sup> as well as to respiration by benthic organisms. Pore water CO<sub>2</sub> enrichment may also be due to surf formation and evaporation and sinking of CO<sub>2</sub>-enriched water into pore spaces in ITZ. Despite the sandy nature, ITZ sediments were found to be rich in benthic productivity and other organisms such as burrowers<sup>5</sup>. Respiration by these organisms could largely be responsible for CO<sub>2</sub> accumulation in ITZ water during low tides (Fig. 2). The highest TCO<sub>2</sub> in pore water occurred at night (2330 hrs) rather than during day time, with a difference of > 200 μmol.dm<sup>-3</sup> (Fig. 2B). Surf zone diatoms respire at night and hence add more CO<sub>2</sub> to pore water than during the day (Dr. Bopaiah Biddanda, Te-

xas A & M University, USA, personal communication) which resulted in higher accumulation.  $\text{TCO}_2$  contents were significantly higher in Expt. I than in Expt. II (Fig. 2) which are due to intensified turbulence during spring tides, since the full moon day occurred 2 days before the Expt. I. The decreasing  $\text{TCO}_2$  abundance towards Expt. II from Expt. I was gradual as another measurement made on 9th October yielded intermediate  $\text{TCO}_2$  concentrations, compared to the levels in Fig. 2, of 1900 and 2042  $\mu\text{mol}\cdot\text{dm}^{-3}$  for NSZ and ITZ water, respectively. Consequently, low  $\text{CO}_2$  noted during Expt. II was a result of decreased tidal amplitude. Variations in temperature and salinity were minimal not only between water of ITZ and NSZ but over the period of this study and hence  $\text{TCO}_2$  changes could not have been resulted from variations in these parameters. The time lag for the occurrence of peaks in  $\text{TCO}_2$  of NSZ (Fig. 2) from peak high tides, was lower during Expt. I as compared to Expt. II. This suggests the inverse relationship between the time lag of  $\text{CO}_2$  transportation and the tidal amplitude. Moreover,  $\text{TCO}_2$  peaks at NSZ are not related to peaks in wind speed confirming the

seaward supply of  $\text{CO}_2$  from ITZ with retreating tidal currents.

Carbon dioxide enrichment in ITZ water compared to that in NSZ water occurs because of upward diffusion of  $\text{CO}_2$  enriched pore water (due to the build up of respired  $\text{CO}_2$  from bacteria and burrowers) and  $\text{CO}_2$  absorption from air due to increased wave action and surf formation. The  $\text{TCO}_2$  enrichment here is quantified as  $\Delta\text{TCO}_2$  ( $=\text{TCO}_2$  in ITZ water  $-\text{TCO}_2$  in NSZ water).  $\Delta\text{TCO}_2$  was positively linearly related to the  $\text{CO}_2$  abundance in air, except when atmospheric  $\text{CO}_2$  was maximum at 0830 hrs during Expt. II (Fig. 3A), irrespective of the wind direction. The absorption can be chemical and diffusional wherein the latter mechanism dominates over the former in the sea<sup>6</sup>. However, when  $\Delta\text{TCO}_2$  was related to atmospheric  $\text{CO}_2$  flux (a product of  $\text{CO}_2$  concentration in air and wind speed) at the sea-land boundary (Fig. 3A), wind direction was noticed to play an important role. Two negative relations noticed in this case were: one for the period when the wind blew from sea to land and the other when the wind direction was reversed, i.e. east to west (Fig. 3A). The negative relations observed in Fig. 3A hence seem to be functions of atmospheric  $\text{CO}_2$  sources which otherwise may have resulted in a single relation instead of two.

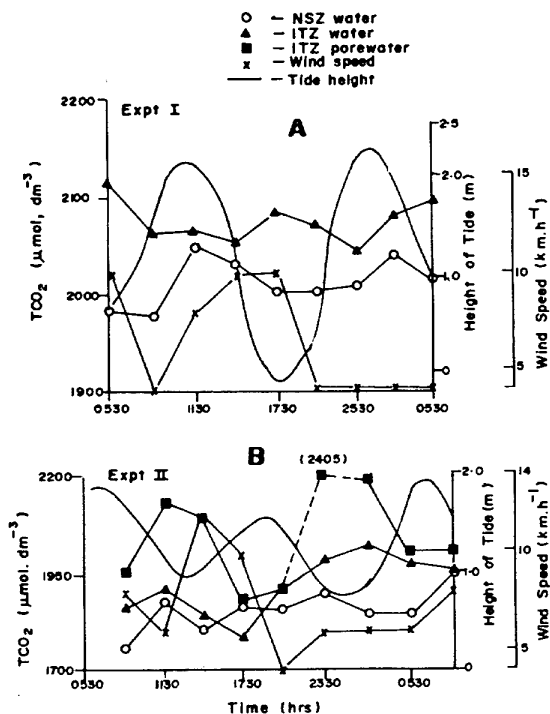


Fig. 2—Diel variations in total carbon dioxide ( $\text{TCO}_2$ ) in intertidal zone (ITZ) and nearshore zone (NSZ; 8m deep and 50m away from ITZ) water and tide height (A) Expt. I and (B) Expt. II

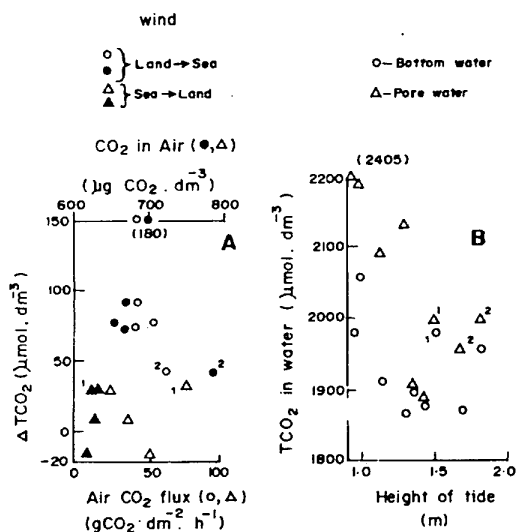


Fig. 3—(A) Relations for  $\Delta\text{TCO}_2$  ( $=\text{TCO}_2$  in ITZ water  $-\text{TCO}_2$  in NSZ water) with  $\text{CO}_2$  in air and atmospheric  $\text{CO}_2$  flux. [(1) maximum wind velocity of  $12\text{ km}\cdot\text{h}^{-1}$  and (2)  $\text{CO}_2$  of 401 ppmv in air occurred], (B) relations for  $\text{TCO}_2$  in bottom and pore water with the height of the tide near ITZ [(1) Change in wind direction from east to west to northeast to southwest occurred and (2) as in Fig. 3A]

To find the influence of wave action on  $\text{TCO}_2$  in ITZ, filtered water samples of overlying, bottom and pore water were collected at times of rise and subsidence of waves on 9th October. While the pore water  $\text{TCO}_2$  was unchanged at  $2205 \mu\text{mol.dm}^{-3}$ , overlying and bottom water contained  $2042$  and  $2057 \mu\text{mol.dm}^{-3}$ , respectively, when the wave was rising but during subsidence it was found to be  $2030$  and  $2042 \mu\text{mol.dm}^{-3}$  respectively. This observation reveals that with the increasing wave height and turbulence, close to sediment-water interface during wave rise, relatively more  $\text{TCO}_2$  was released to the water column in relation to that during wave subsidence. Increased diffusivity near sediment surface is related to small scale turbulence caused by bottom swell and tidal currents<sup>7</sup>. The upward diffused  $\text{CO}_2$  during wave rise should have been diluted to some extent when the wave height reached maximum, before carrying  $\text{TCO}_2$  seaward during subsidence. Figure 3B depicts inverse relations for height of the tide with  $\text{TCO}_2$  in bottom and pore water, in general. The decreasing efficiency of water flow pulses in and out of pore spaces with increasing water depth<sup>8</sup> results in the  $\text{TCO}_2$  dilution. However, the difference between  $\text{TCO}_2$  of overlying and bottom water indicates the

upward diffusion of  $\text{CO}_2$  from pore water. This substantiates the facts observed in Fig. 2 that  $\text{TCO}_2$  enriched water, that occurred because of the upward diffusion of pore water  $\text{CO}_2$  during the tidal increase, in the ITZ is being carried offshore when the tides recede.

#### Acknowledgement

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