Deep-Sea Research II 118 (2015) 177–185

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Stable isotopic signature of Southern Ocean deep water CO_2 ventilation

K. Prasanna[a], Prosenjit Ghosh[a,b,*], N. Anil Kumar[c]

[a] Centre for Earth Sciences (CEaS), Indian Institute of Science, Bangalore 560012, India
[b] Divecha Centre for Climate Change, Indian Institute of Science, Bangalore 560012, India
[c] National Centre for Antarctic and Ocean Research, Headland Sada, Goa 403804, India

ARTICLE INFO

Available online 25 April 2015

Keywords:
Southern Ocean
CO_2
Deep water ventilation
DIC
$\delta^{13}C$

ABSTRACT

The link between atmospheric CO_2 level and ventilation state of the deep ocean is poorly understood due to the lack of coherent observations on the partitioning of carbon between atmosphere and ocean. In this Southern Ocean study, we have classified the Southern Ocean into different zones based on its hydrological features and have binned the variability in latitudinal air-CO_2 concentration and its isotopic ratios. Together with air-CO_2, we analysed the surface water for the isotopic ratios in dissolved inorganic carbon (DIC). Using the binary mixing approach on the isotopic ratio of atmospheric CO_2 and its concentration, we identified the $\delta^{13}C$ value of source CO_2. The isotopic composition of source CO_2 was around $-9.22 \pm 0.26‰$ for the year 2011 and 2012, while a composition of $-13.49 \pm 4.07‰$ was registered for the year 2013. We used the $\delta^{13}C$ of DIC to predict the CO_2 composition in air under equilibrium and compared our estimates with actual observations. We suggest that the degeneration of the DIC in presence of warm water in the region was the factor responsible for adding the CO_2 to the atmosphere above. The place of observation coincides with the zone of high wind speed which promotes the process of CO_2 exsolution from sea water.

1. Introduction

Fossil fuel emissions during the industrial era were found responsible for the increase in air-CO_2 concentration from its preindustrial value of ~280 PPMV to the present day concentration of ~400 PPMV. This led to an overall increase in the global mean temperatures by approximately 0.76 °C ± 0.19 °C (IPCC, 2007). The global ocean currently absorbs annually about 2 Pg C yr^{-1} (1 Pg = 1 petagram = 10^{15} g = 1 billion tons) of CO_2 from the air (Takahashi et al., 2012). The rate of absorption of CO_2 generated due to natural and anthropogenic emissions (e.g. fossil fuel burning, cement manufacture, and gas flaring) played a significant role in defining the residence time of CO_2 in the atmosphere. The CO_2 thus emitted stayed in the atmosphere for a duration of 5–200 years until it was scavenged by either land biosphere or oceanic sinks. However, the rate of exchange of CO_2 varies significantly between land and ocean. The Southern Ocean (SO), demarcated by the oceanic region south of 44°S is unique as it has been identified as a major sink of global carbon accounting for 1 Pg C yr^{-1} which is close to 50% of the CO_2 emitted into the atmosphere (Caldeira and Duffy, 2000; Fletcher et al., 2006). Projections suggested that the region will continue to be an important sink of atmospheric CO_2, although the rate of sinking might decrease in the future (Roy et al., 2011). The process of CO_2 uptake in the SO is poorly understood due to the lack of data; however the role of temperature and wind in the process of CO_2 uptake is well documented in the literature (Longinelli et al., 2012). The uptake of CO_2 occurs through a combination of biological and physical processes. Even though the SO has a net negative flux of CO_2 per year, there are certain zones in the SO where the net flux of CO_2 is positive during summer (Metzl, 2009). Wind stress has a positive role in driving the variations in CO_2 fluxes (Anderson et al., 2009; Waugh, 2014; Waugh et al., 2013). CO_2 efflux in the SO is important because it is regarded as a High Nutrient Low Chlorophyll (HNLC) region where the chlorophyll biomass remains low, despite an abundant supply of the major nutrients (Martin et al., 2013). The poorly utilised nutrients in the region of the SO have important implications for the global carbon cycle. The process of assimilating inorganic carbon (atmospheric CO_2) into organic matter during photosynthetic pathways and its subsequent conversion to organic carbon during burial, and inorganic carbon by means of heterotrophic respiration and re-equilibration with atmospheric CO_2, is collectively referred to as the "biological pump". This pump is one of the factors responsible for maintaining DIC concentrations and atmospheric CO_2 concentration over the SO. However, the HNLC water of the SO represents an "open window" through which a CO_2 efflux is possible, thus

---

* Corresponding author at: Centre for Earth Sciences (CEaS), Indian Institute of Science, Bangalore 560012, India.
E-mail address: pghosh@ceas.iisc.ernet.in (P. Ghosh).

http://dx.doi.org/10.1016/j.dsr2.2015.04.009
0967-0645/

reducing the efficiency of the biological pump. Hence it is important to study the SO for the zone of CO_2 efflux and characterise the source.

In this paper, we present observations on atmospheric CO_2 concentration, the $\delta^{13}C$ in atmospheric CO_2 sampled in the glass flask and the $\delta^{13}C$ of DIC in sea surface water samples collected across the latitudes over the Indian sector of the SO during the year 2011, 2012 and 2013. The intercept value in the plot of $\delta^{13}C$ in atmospheric CO_2 and $1/CO_2$ concentration, popularly known as the Keeling's mixing model (Keeling, 1958), was used to trace the source. We have also discussed the role of wind influencing the CO_2 venting from the SO.

2. Hydrological and biogeochemical context

2.1. Major hydrological fronts and water masses

Several researchers have demarcated major hydrological fronts and zones of water masses over the SO based on sharp contrasts in the temperature, salinity and productivity (Eynaud et al., 1999; Sparrow et al., 1996). For ease of understanding, we demarcated the entire SO into four fronts which were named: The Agulhas Retroflection Front (ARF) which covers the latitude from 38°S to 39°S and is characterised by a drop in temperature and salinity from 19.6 °C to 18.8 °C and 35.7 to 35.5; the Sub Tropical Front (STF) which lies between 40°S and 42°S and isolates the warmer tropical water from the cooler subtropical water where the temperature drops from 18.7 °C to 12 °C, and the salinity drops from 34.11 to 33.8; the Sub Antarctic Front (SAF) which covers latitudes from 45°S to 48°S and is characterised by a drop in salinity level from 33.9 to 33.8 and the temperature drops from 10.5 °C to 6.3 °C and the Polar Front (PF) which extends from 49°S till 56°S where the salinity values fall in narrow range of 33.8–33.9 while the temperature varies from 4.8 °C to 3.1 °C (Anilkumar et al., 2005; Srivastava et al., 2007). These zones, marked by the sea surface temperature and salinity changes were easily traceable on the surface (Srivastava et al., 2007) and remained nearly similar during the austral summers of the years 2011, 2012 and 2013 as shown in Fig. 1.

2.2. Biogeochemical regions.

Across the meridional transect, the SO is broadly classified into five biogeochemical zones (Pollard et al., 2002; Racape et al., 2010) based on productivity and temperature. This includes the Tropical Indian Ocean (TIO) which extends from 20°N to 20°S, the Sub-Tropical Zone (STZ) between 20°S and 35°S, the Transition Zone (TZ) between 35°S and 40°S, the Sub-Antarctic Zone (SAFZ) between 40°S and 45°S, the Polar Frontal Zone (PFZ) between 45°S and 50°S, and the Antarctic Zone (AAZ) beyond the south of 50°S.

3. Material and methods

The work presented here is based on the $\delta^{13}C$ and concentration measurement of air-CO_2 and the $\delta^{13}C$ measurement of DIC measured on the air and water samples collected at intervals across the SO on-board ORV *Sagar Nidhi* on three expeditions coinciding with the austral summers of 2011, 2012 and 2013. The sampling stations are marked in Fig. 2.

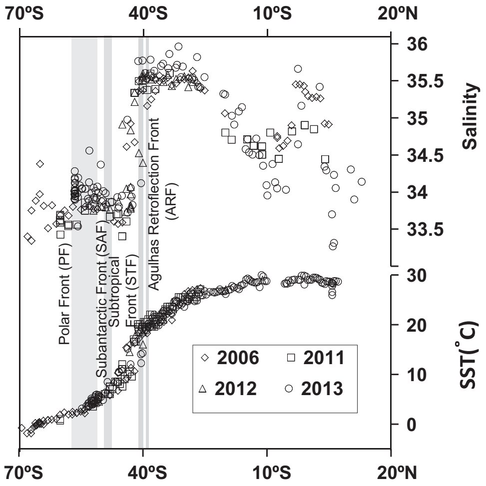

Fig. 1. Variation in salinity and temperature of sea water (SST till 75 m water depth) across the Southern Ocean is shown in this plot. The data recorded during the Southern Ocean expedition 2011, 2012 and 2013 are compared with observations from the previous study in the same region (Srivastava et al., 2007). Note the large shift in salinity and temperature in the region lying between latitudes 40°S and 55°S, while the inter-annual variability of the positions of different fronts was negligible.

3.1. $\delta^{13}C$ and concentration measurement of air-CO_2

Air samples were collected once in a day at different stations (mentioned in Table 1) when the sky was clear. The samples were stored in glass flasks of three litre capacity after ensuring complete removal of moisture using a trap filled with Mg $(ClO_4)_2$. The individual flasks were conditioned with sample air using an external pump (NMP 850 KNDC.KNF Neuberger, Freiburg, Germany) operated with a 12 V battery, where 15 min of flushing time was given at a flow rate of 4.5 l/min. The final pressure of ~1.2 bar was achieved after the complete filling of air in the flask. CO_2 from the air samples were extracted using the cryogenic extraction procedure described in (Guha and Ghosh, 2013) for $\delta^{13}C$ analysis in an Isotope ratio mass spectrometer (Thermo Fisher- MAT 253) with dual inlet peripheral. The standard primary carbonate NBS-19 and internal air reference material, 'OASIS AIRMIX'(Guha and Ghosh, 2013) were analysed intermittently to check the consistency and reproducibility of the analyses. JRAS 06, which is a multi-point scale anchor for isotope measurements of CO_2 in air (Wendeberg et al., 2013) was analysed together with air samples to express the delta values of air-CO_2 samples in the VPDB scale (shown in Supplementary Fig. 1). An offset correction was incorporated for the presence of N_2O in the sample air and the inconsistency detected while analysing the JRAS 06 reference air.

The CO_2 concentration was measured using two different approaches; during the year 2011, CO_2 mixing ratios were measured using a Gas Chromatograph (Thermo Fisher - Chemito GC 8610), whereas for other years 2012 and 2013, the CO_2 mixing ratios were determined using a gravimetric technique. Gas Chromatography method involves the separation of CO_2 from other components by passing an aliquot of an air sample through a CP-Pora PLOT Q column and analysing the CO_2 by a methanizer with a Flame Ionization Detector (FID). The Gravimetric method involves the cryogenic extraction of CO_2 followed by the transfer of CO_2 to an ampoule with known volume, where the pressure was accurately measured using a MKS Baratron at a temperature of 25°C. The value was further converted to number of micro moles of CO_2 using the pressure volume relationship of the ideal gas law ($pV=nRT$). By knowing the number of moles of the air sample, the CO_2 mixing ratio was calculated based on the volume of sample air in the flasks and initial and final pressure in the flask