Distribution and air–sea exchange of nitrous oxide in the coastal Bay of Bengal during peak discharge period (southwest monsoon)

G.D. Rao, V.D. Rao, V.V.S.S. Sarma *

CSIR-National Institute of Oceanography, Regional Centre, 176 Lawson's Bay Colony, Visakhaptnam 530 017, India

A B S T R A C T

In order to examine the impact of river discharge from the Indian subcontinent on the concentration and air–sea exchange of nitrous oxide (N_2O) a study was conducted during peak discharge period in the coastal Bay of Bengal, The study revealed that freshwater discharge exerts a dominant control on the N_2O cycling in the surface waters of the coastal Bay of Bengal. The surface concentration of N_2O in the southwestern (SW) coastal Bay of Bengal was high (7.4 ± 1.6 nM) and supersaturated ($126 \pm 27\%$) whereas contrasting trend was found in the northwestern (NW) region (4.9 ± 0.3 nM and $81 \pm 6\%$). Such spatial differences in N_2O concentration and saturation were resulted from variable characteristics of the discharged waters, and vertical stratification. The NW region of the coastal Bay of Bengal was under the influence of the discharge from the Ganges River having N_2O below the saturation in the estuary ($82 \pm 5\%$) while the SW region was under the influence of peninsular river discharges that were super-saturated ($187 \pm 29\%$). The low N_2O concentration at NW region resulted from low concentrations in the source water (Ganges) as these waters were formed by melting of the Himalayan glacier where low ammonium concentrations were observed due to less human settlement resulting in lower nitrification rates. Higher concentration of N_2O in the SW region was attributed to the discharge from monsoonal rivers containing high N_2O concentrations, high nitrification rates and mild coastal upwelling. The sea-to-air fluxes of N_2O suggest that NW region is a sink for atmospheric N_2O due to discharge of under saturated water from Ganges and strong stratification while SW region is a source caused by coastal upwelling and discharge of highly saturated water from monsoonal rivers.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Nitrous oxide (N_2O) is an important greenhouse gas having very long residence time in the atmosphere (100–150 years) compared to other greenhouse gases. N_2O is involved in generating stratospheric NO, which contribute to the net destruction of stratospheric ozone (Crutzen, 1970; Nevison and Holland, 1997). The atmospheric mixing ratio of the N_2O (325 ppbv) is smaller than that of carbon dioxide (CO_2; 395 ppmv; http://www.esrl.noaa.gov/gmd/), by ~1000 times, however, the greenhouse potential of N_2O is ~300 times higher than that of carbon dioxide (CO_2) (Forster et al., 2007). The radiative forcing, due to increase in greenhouse gas concentrations from the pre-industrial (1750 to 2011) is estimated to be $+2.839$ Wm^{-2} (comprising CO_2 (1.817 Wm^{-2}), CH_4 (0.506 Wm^{-2}), N_2O (0.178 Wm^{-2}) and halocarbons (0.338 Wm^{-2})), with an uncertainty of 10%. Intensification of fossil fuel combustion and nitrogenous fertilizer application since the pre-industrial era has increased global emission of N_2O (Bange et al., 2010; Suntharalingam et al., 2012). The N_2O concentration in the atmosphere is increasing steadily, ca 0.2–0.3% y^{-1} on average that raises concerns about future global climate change (Khalil and Rasmussen, 1992; Houghton et al., 2001; Doney et al., 2007; Duce et al., 2008).

N_2O can be formed through processes naturally as well as by anthropogenic activities (Suntharalingam et al., 2012). N_2O is formed under both reductive and oxidative conditions by bacteria during denitrification of nitrate (Knowles, 1996) and nitrification of ammonium ion (Yoh et al., 1988) in the marine environment. Denitrification occurs mainly in the suboxic environment and nitrification in the oxygen rich environment such as the well ventilated surface (Codispoti et al., 2001; Naqvi et al., 2000, 2010). The atmospheric budget of N_2O is greatly influenced by its production in the ocean and exchange across the air–sea interface as the oceans are estimated to account for at least one-third (1.2–6.8 Tg N_2O y^{-1}) of N_2O inputs to the atmosphere from all natural sources (~11 Tg N_2O y^{-1}; Nevison et al., 1995; Prather et al., 2001; Suntharalingam and Sarmiento, 2000; Ishijima et al., 2010). The recent IPCC synthesis report suggests that flux of N_2O from the rivers, estuaries and coastal waters represents about 22% of the total anthropogenic N_2O source and about 10% of the total source (http://www.ipcc.ch/). On the other hand, the natural sources from the open ocean accounts 35% of the total natural source and about 21% of all sources (natural and anthropogenic). However,

---

* Corresponding author. Tel.: +91 8912744799.
E-mail address: sarmav@nio.org (V.V.S.S. Sarma).

these estimates carry significant amount of uncertainties due to lack of systematic data from several regions. Bange et al. (1996) noticed that coastal water contributes up to 60% to the total marine emissions. However, N$_2$O emissions are not uniformly distributed over the ocean surface as tropical upwelling zones containing oxygen deficient waters make a disproportionately large contribution (Codispoti and Christensen, 1985; Suntharalingam et al., 2000; Codispoti et al., 2001). N$_2$O cycling mechanisms display sensitivity to the variations in dissolved oxygen concentration and higher yields are noted at low oxygen levels and ascribed to alternate pathways such as enhanced nitrification, denitrification and interactions between the two (Yoshida et al., 1989; Codispoti et al., 2001; Naqvi et al., 2000). In addition to this, denitrification that occurs at low dissolved oxygen concentration, acts as sink for N$_2$O in the water column (Codispoti et al., 2001; Naqvi et al., 2000).

Based on reported data for the European coastal areas (i.e. Arctic Ocean, Baltic Sea, North Sea, northeastern Atlantic Ocean, Mediterranean Sea, and Black Sea), Bange (2006) reassessed dissolved concentrations and atmospheric emissions of N$_2$O. Maximum N$_2$O saturations were found in estuarine systems, whereas the shelf waters, which are not influenced by freshwater plumes, are close to equilibrium with the atmosphere. More recently Barnes and Upstill Goddard (2011) estimated air–sea exchange of N$_2$O from the UK estuaries and estimated that the mean fluxes from the European estuaries to be 2.7 µmol N$_2$O m^{-2} d^{-1}. They concluded that the water column nitrification is the major source of N$_2$O in the European estuaries. This implies that N$_2$O is mainly sourced from the estuarine systems.

The northeastern Indian Ocean (Bay of Bengal) receives excessive precipitation over evaporation. It also receives a huge amount of freshwater (1.6 × 10^{12} m^3 y^{-1}; UNESCO, 1979) from the major rivers such as Ganges (0.44 × 10^{12} m^3 y^{-1}), Godavari (0.11 × 10^{12} m^3 y^{-1}), Krishna (0.07 × 10^{12} m^3 y^{-1}) and Mahanadi (0.06 × 10^{12} m^3 y^{-1}; Kumar et al., 2005) etc. Both precipitation and river discharge peak during southwest (SW) monsoon (June–September). Very few observations have been carried out so far on the distribution of N$_2$O in the atmosphere and waters in the Bay of Bengal. Naqvi et al. (1994) measured along the west coastal Bay of Bengal during March–April 1991 whereas Hasimoto et al. (1998) in the central Bay of Bengal during February 1995 and 1996. Their study revealed that surface N$_2$O saturation and atmospheric fluxes ranged from 70.6 to 253% (mean 106%), and −70.8 to 175.3 µmol (N$_2$O) m^{-2} d^{-1} (mean 0.78 µmol m^{-2} d^{-1}), respectively. The overall N$_2$O flux from the Bay of Bengal was estimated to be 0.027–0.077 Tg N yr^{-1} which is substantially lower than that computed for the Arabian Sea (0.33–0.70 Tg N yr^{-1}; Bange et al., 2001). Lower surface saturations and consequently smaller air–sea fluxes in the Bay of Bengal were attributed to strong stratification caused by the immense river runoff. However, the budget estimates may be biased due to lack of seasonal data.

Recently Sarma et al. (2011) observed record levels of pCO$_2$ (>30,000 µatm) in the largest monsoonal estuary in India, Godavari, during peak discharge period whereas other monsoonal estuaries are also a significant source to atmosphere during discharge period (Sarma et al., 2012a). The nutrient levels in the monsoonal rivers were also significantly higher during discharge period (Sarma et al., 2010). The discharge of these nutrients and pCO$_2$ rich waters to the coastal region has significant impact on coastal biogeochemistry (Sarma et al., 2012b). The characteristics of rivers opening into the Bay of Bengal are influenced by activities of local population, terrain characteristics, industrial activities, and pollution levels etc. that are widely variable. No observations have been carried out so far along the east coast of India during peak discharge period to understand how discharges from different rivers influence coastal N$_2$O fluxes. The aim of this study is to understand the influence of major peninsular rivers along the east coast of India on N$_2$O concentrations and their fluxes at the air–water interface in the coastal Bay of Bengal during southwest monsoon (SWM)/peak discharge period.

2. Material and methods

2.1. Study area

Samples were collected on board ORV Sagar Nidhi (#SN 42) during 23rd July to 10th August 2010, representing peak SW monsoon and high river discharge period, along the east coast of India covering major rivers such as Krishna (KS, KN transects), Godavari (GS, GN) and Mahanadi (MS, MN) and minor rivers, Vamsadara (VD) and Hyadri (HD) (Fig. 1). Seventy three stations were occupied in 9 transects covering both south (S) and north (N) of riverine mouths of major rivers. Transect V (off Visakhaptnam city) was chosen to represent no discharge location. Samples were collected from coast to ~70–100 Kilometers offshore. Samples were also collected in the estuaries of the rivers Krishna, Godavari, Mahanadi and Ganges during the same time of coastal sampling to examine the characteristics of the discharging water into the coastal Bay of Bengal. About 3–5 samples were taken using mechanized boat in the estuaries covering about 10 km from the estuarine mouth to upstream estuary. In order to represent spatial variations along the coastal Bay of Bengal, the data were conveniently divided to represent northwestern (NW) (includes data from VD, HD, MN, and MS transects) and southwestern (SW) region of the coastal Bay of Bengal (includes data from KS, KN, GS, GN and V transects).

2.2. Sampling and analyses

2.2.1. Hydrographic parameters

Water samples were collected using a Seabird Conductivity–Temperature–Depth (CTD)-rosette system fitted with 5 l Niskin bottles. Analysis for nutrients (nitrate, nitrite, ammonium, phosphate and silicate) and dissolved oxygen (DO) was completed shortly after the collection of samples. DO was estimated by potentiometric method following Carritt and Carpenter (1966) using Titrando 835 Metrohm autotitrator. Nutrients were analyzed following standard procedures (Grashoff et al., 1992) using auto analyzer. The analytical precision, expressed as standard deviation, was ±0.07% RSD for DO whereas for nitrate + nitrite, ammonium, phosphate and silicate were ±0.02, 0.02, 0.01 and 0.02 µM respectively. A volume of 2 to 5 l of water sample was filtered through GF/F filter (Whatman) and phytoplankton biomass retained on filter was extracted with N,N-dimethylformamide (DMF) for Chlorophyll-a at 4 °C in the dark for 12 h, and then analyzed spectrofluorometrically (Varian Eclipse Fluorescence spectrophotometer, USA) following Suzuki and Ishimaru (1990). The analytical precision for Chl-a analysis was ±4%. The suspended particulate matter (SPM) was measured based on weight difference of the material retained on 0.22 µm pore size polycarbonate filters after passing 1 l of sample. Winds were measured continuously along the ship's cruise track using automated weather station (AWS) installed on the ship at 13.5 m above. River discharge data were obtained from dam authorities of the respective river.

2.2.2. Measurements of N$_2$O

The water samples for N$_2$O were collected in 60 ml amber colored bottles immediately following the sampling of DO. Samples were poisoned with 0.5 ml of saturated HgCl$_2$ to prevent microbial activity. The samples were analyzed within 2 h after collection on board. N$_2$O dissolved in the water was determined by a multiphase head space equilibration technique (McAuliffe, 1971) coupled with gas chromatographic (GC) analysis. Briefly, predetermined volume (25 ml) was equilibrated with equal volume of ultra pure helium in a gas tight syringe by vigorously shaking the syringe at room temperature for 5 min using wrist action shaker. After equilibrium, the head space was dried over Drierite and then injected through a 5-ml sampling loop into a gas chromatograph (Agilent-6820, USA) and separated over a chromosorb column (80/100 mesh) at 35 °C, and N$_2$O peak was