Distributions and sea-to-air fluxes of nitrous oxide in the South China Sea and the West Philippines Sea

Hsiao-Chun Tseng a, b, Chen-Tung Arthur Chen b, *, Alberto V. Borges c, T. Angel DelValls a, Chao-Ming Lai d, Ting-Yu Chen b

a UNESCO Unitwin/WICop, Physical Chemistry Department, Faculty of Marine and Environmental Sciences, Polígono río San Pedro s/n, University of Cadiz, 11519 Puerto Real, Cadiz, Spain
b Department of Oceanography, National Sun Yat-sen University, Kaohsiung 804, Taiwan
c Université de Liège, Unité d’Océanographie Chimique, Institut de Physique (BS), B-4000, Belgium
d Department of Agricultural Chemistry, National Taiwan University, Taipei 106, Taiwan

Abstract

Approximately 600 water samples from the South China Sea (SCS) and 250 water samples from the West Philippines Sea (WPS) were collected during seven cruises from August 2003 to July 2007 to determine nitrous oxide (N₂O) distributions between the surface and a maximum depth of 4250 m. In the SCS, the average surface N₂O concentration exceeded the atmospheric equilibrium concentration (on average 132 ± 23%); however in the WPS, the surface N₂O concentration was lower than the atmospheric equilibrium concentration (on average 90 ± 22%). The N₂O concentration reached a maximum (~23 nmol L⁻¹) in the WPS at 800–1000 m, and (~28 nmol L⁻¹) at a shallower depth of around 600–800 m in the SCS, owing to vertical mixing and intensive upwelling in the SCS. In the SCS, the surface N₂O concentration was 7.59 ± 1.32 nmol L⁻¹ and the calculated sea-to-air flux was 5.5 ± 3.9 μmol m⁻² d⁻¹. The surface N₂O concentration in the WPS, 5.19 ± 1.26 nmol L⁻¹, was lower than that in the SCS. The WPS is a sink for N₂O and the calculated sea-to-air flux was ~1.7 ± 3.9 μmol m⁻² d⁻¹. The SCS emitted 19.3 × 10² mol d⁻¹ N₂O to the atmosphere and exported 8.5 × 10⁶ mol d⁻¹ N₂O to the WPS during the wet season.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Nitrous oxide (N₂O) is a trace gas that strongly influences the climate and atmospheric chemistry. It is a long-lived and powerful greenhouse gas (Prather et al., 2012), ranking third in anthropogenic radiative forcing, only behind carbon dioxide (CO₂) and methane (CH₄) (Myhre et al., 2013). Additionally, N₂O has a global warming potential in a 100-year time frame (GWP100) that is 298 times that of CO₂ (IPCC, 2013). Atmospheric concentrations of N₂O have risen from 270 ± 7 ppb in 1750–324.2 ± 0.1 ppb in 2011 (IPCC, 2013). The gas also affects the climate by interacting with the stratospheric ozone (Crutzen, 1974; Nevison and Holland, 1997; Prather et al., 2001) as the N₂O in the stratosphere is an important precursor of nitric oxide (NO) radicals, which are involved in the depletion of the atmospheric ozone (Crutzen, 1970; Ravishankara, et al., 2009). Since 2011, N₂O has become the dominant ozone-depleting substance on account of the decrease in the impact of dichlorodifluoromethane (CFC-12) after the implementation of the Montreal Protocol and amendments (Ravishankara et al., 2009).

Natural sources of N₂O include oceans, sediments, inland waters, and terrestrial soils. However, global inventories of these sources are still fairly uncertain. According to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC 5AR), the oceans are significant sources of the atmospheric N₂O, and account for approximately one-third of global natural emissions and one-fifth of total (natural and anthropogenic) emissions. Nevison et al. (1995) computed a global ocean source of 4 Tg N yr⁻¹, with a large range of uncertainty from 1.2 to 6.8 Tg N yr⁻¹ based on 60,000 at-sea measurements. Model-derived estimates also vary widely, between 1.7 and 8 Tg N yr⁻¹ (Nevison et al., 2003; Suntharalingam and Sarmento, 2000). Recently, Manizza et al. (2012) used a large-scale ocean general circulation model that was coupled with a biogeochemical model to quantify mean ocean emissions at 4.5 TgN yr⁻¹, while Saikawa et al. (2014) estimated an oceanic N₂O source with a flux of between 3.6 and 5.2 TgN yr⁻¹, based on a global atmospheric inversion model. These large uncertainties arise from too few observations and poor...
knowledge of mechanisms of N₂O formation, reflecting a general lack of understanding of key aspects of the oceanic nitrogen cycle (Gruber and Galloway, 2008; Zehr and Ward, 2002), and of N₂O in particular (e.g., Bange et al., 2009; Freing et al., 2012; Zamora et al., 2012, among others).

Most N₂O in oceanic environments is formed from NH₂OH as a byproduct of nitrification (NH₄⁺ → NH₂OH → NO₂⁻ → NO₃⁻) and as an intermediate product during denitrification (NO₃⁻ → NO₂⁻ → N₂O → N₂). During autotrophic nitrification N₂O can be formed by NH₄⁺ → NH₂OH (→ NO) → NO₂⁻ either via the pathways NH₂OH → N₂O and NO → N₂O (Arp and Stein, 2003; Stein and Yung, 2003) or via the pathway NO₂⁻ → NO → N₂ (the latter is part of the so-called nitrifier-denitrification process) (Stein and Yung, 2003; Wrage et al., 2001). Nitrification is believed to be the main contributor to the production of N₂O in seawater (Najjar, 1992; Bange and Andreae, 1999; Freing et al., 2012). Denitrification occurs under low oxygen (< 6 μmol L⁻¹) to anoxic conditions (Nevison et al., 2003). Denitrification produces and consumes N₂O in oxygen minimum zones and the net result is that oxygen minimum zones have some of the highest N₂O concentrations in the ocean (LaMontagne et al., 2003; Naqvi et al., 2010; Zamora et al., 2012; Arévalo-Martínez et al., 2015). In the water column with low oxygen concentrations and in sediments or inside suspended particles, nitrification and denitrification can occur simultaneously and are often closely coupled (Seitzinger, 1988; Ward et al., 1989; Capone, 1991; Middelburg et al., 1996; Barnes and Owens, 1998; Naqvi et al., 1998; Robinson et al., 1998; Usui et al., 2001; Nevison et al., 2003; Codispoti et al., 2005; Bange, 2008). The yield of N₂O from both processes is highly dependent on the concentration of dissolved oxygen (Goreau et al., 1980; de Bie et al., 2002; Naqvi et al., 2010).

Few investigations of N₂O in the South China Sea (SCS) have been published, and these have only considered the northern part (Xu et al., 2006; Zheng et al., 2009; Han et al., 2013). Almost no data on N₂O in the West Philippines Sea (WPS) are available. This paper presents the spatial and vertical distributions of N₂O in the water columns of the SCS and the WPS as well as the sea-to-air fluxes. The differences between these seas and the influencing factors are discussed. Additionally, previous research in the SCS calculated the excess N₂O (ΔN₂O) concentration by using “the contemporary atmospheric mole fraction” throughout the water column. This study for the first time calculates the ΔN₂O by using “the initial atmospheric mole fraction” to reduce the uncertainty of ΔN₂O.

2. Study area

The SCS is the largest marginal sea in the world with an area of 3.5 × 10⁶ km² and an average depth of 1350 m. At the southern edge of the SCS lies the Sunda Shelf, which has a mean depth of around 50 m and is connected to the Straits of Malacca. The Mindoro Strait connects the eastern SCS with the Sulu Sea and the Taiwan Strait connects the northern SCS with the East China Sea. The northeastern SCS is connected with the WPS via the Luzon Strait, which has the deepest sill of any that connects the SCS with any adjacent bodies of water. As the Luzon Strait is 2200 m deep, the surface and intermediate waters are exchanged freely between the SCS and the WPS. Whereas waters that are deeper than 2200 m in the WPS cannot enter the SCS. Consequently, waters deeper than 2200 m in the SCS are relatively homogeneous, with hydrochemical properties that are similar to those of the water at 2200 m in the WPS (Chen et al., 2006).

The WPS is located in the western part of the North Pacific with an average depth of around 5500 m, and it is bordered by the Japanese islands of Honshu, Shikoku, and Kyushu to the north, the Ryukyu Islands to the northwest, Taiwan to the west, the Philippine archipelago to the south, and the Izu-Ogasawara Ridge and the Mariana Ridge to the east. The Kyushu-Palau Ridge (at a longitude of around 135°E) separates the West Mariana Basin from the WPS. This study focuses on the region between 120.5°E and 126.5°E and between 21°N and 26°N, where the WPS connects with the SCS and a significant quantity of water is frequently exchanged.

The Asian monsoon dominates climatic variations at the sea-air interface of the SCS. The southwest monsoon season runs from May to October and brings extensive precipitation; it is the wet season in Southeast Asia. The northeast monsoon season runs from November to April and is characterized by high wind speeds (Han, 1998). The seven cruises herein were all conducted during the wet season.

3. Materials and methods

3.1. Sample collections

Samples were taken during five cruises on board R/V Ocean Researchers I and III in the SCS (Fig. 1a; Table 1), designated ORIII-896 (August 2003), ORI-695 (September 2003), ORIII-983 (July 2004), ORI-802 (July 2006), and ORI-837 (July 2007).

Samples were collected close to the south of the Taiwan Strait, which is located in the northeastern part of the SCS, during the cruises in August 2003 (ORIII-896) and July 2004 (ORIII-983). ORI-695 was conducted near the Pearl River estuary and was influenced by the summer estuarine plume (Han et al., 2012; Zhai et al., 2013; Bai et al., 2015). The Pearl River (Zhujiang) is the 13th largest river in the world (Yin et al., 2011) and the second largest river in China (after the Yangtze River) with a water discharge of 326 × 10⁶ m³ annually; it is also the second largest river (after the Mekong River) that enters the SCS (Chen et al., 2008).

In July 2006 (ORI-802), samples were taken on the Sunda Shelf and on the continental slope, where the depth increases sharply. From July 16–31 of 2007 (ORI-837), surface water samples were taken from the Luzon Strait and along the western coast of Luzon Island, Palawan Island, and the western coastal area of Borneo Island; profile water samples were taken at various depths from the eastern part of the SCS to the southern part of the SCS.

Samples were obtained from the WPS during three of the cruises (Fig. 1b; Table 1). Profile water samples were taken at various depths on ORI-725 (August 2004) and ORIII-1149 (May 2006). These two cruises were conducted along 22°N from 120.5°E to 126.5°E in August 2004 and from 120.5°E to 124°E in May 2006, respectively. Surface water samples were taken from the north-eastern coast of Taiwan to the Luzon Strait on ORI-725 (August 2004) and ORI-837 (July 2007).

Water samples were collected from various areas and depths using a Rosette sampler that was fitted with 5 L or 10 L Niskin bottles along with a conductivity–temperature–depth (CTD) probe (Sea-Bird 911, USA). Saturated HgCl₂ was added to all samples to inhibit microbial activity, excluding those that were used to measure salinity. Temperature data were obtained from the CTD profiles, whereas the salinity values that were used in the analysis were determined from discrete AUTOSAL measurements.

Water samples that were used to measure N₂O concentration were collected in 120 ml dark glass bottles. The bottles were rinsed three times using the sampled water. After one fold of bottle volume was allowed to overflow the bottle, 10 ml of the water sample was withdrawn from the bottle to leave an air space and 0.5 ml saturated HgCl₂ was then added. The sample bottles were then immediately sealed with a butyl rubber stopper and an
aluminum cap. The samples were stored in a dark box at 4 °C. All water samples were transferred to a laboratory and analyzed within three months of collection.

3.2 Chemical analysis

The salinity of the water samples was determined by measuring the conductivity using an AUTOSAL salinometer (Guidline Instruments), which was calibrated using the standard seawater (batch no. P141) from the International Association for the Physical Sciences of the Oceans (IAPSO). The precision of the salinity measurements was ± 0.003. Chlorophyll a samples were collected by filtration through a 0.45 μm diameter Millipore polycarbonate filter. A Turner Designs model 10-AU fluorometer (Varian Eclipse) was utilized to measure chlorophyll a concentration following extraction by 90% acetone (Strickland and Parsons, 1972) with a precision of ± 5%. Dissolved oxygen (DO) concentration was measured by the direct spectrophotometry (Pai et al., 1993) with a precision of about ± 0.32% at the 190 μmol L⁻¹ level. The apparent oxygen utilization (AOU) was calculated using the oxygen solubility equation of Chen (1981), as a function of salinity and temperature. Nitrate (NO₃⁻) plus nitrite (NO₂⁻) concentration was measured by the pink azo dye method (Strickland and Parsons, 1972) using a flow injection analyzer and an online Cd coil. The precision of this method was around ± 1% at 35 μmol L⁻¹, and ± 3% at 1 μmol L⁻¹. The NO₂⁻ concentration was also obtained by the pink azo dye method (Strickland and Parsons, 1972; Pai et al., 1990) using a flow injection analyzer, yielding a precision of ± 0.02 μmol L⁻¹.

The concentration of dissolved N₂O was estimated using the modified headspace equilibrium method (Johnson et al., 1990) with gas chromatographs (GC; Varian 3600 and 3800) that were equipped with electron capture detectors (ECD). The samples were placed in a water bath at a constant temperature of 25 °C, and allowed to equilibrate for at least three hours. Two ml of the gas from the headspace was injected into the GC. The GC-ECD had a 3.6 m × 1/8 in. stainless steel column, which was filled with 80/100 mesh Porapak Q. The ECD was calibrated with pure N₂ (Jing-Shang, Taiwan) and two commercial gas mixtures with an N₂O mixing ratio of 1.0 ppmv (Scott Specialty Gases, U.S.A.) and 2.5 ppmv (All-Win, Taiwan). The precision of the repeated routine analysis of water samples was approximately ± 5% of the concentration of N₂O. To acquire the calibration curve, airtight bags were used to mix pure N₂ with two standard gases to reach N₂O concentrations of 0, 0.25, 0.5, 0.75, 1, 1.5, 2, and 2.5 ppmv (All-Win, Taiwan). The precision of this method was around 3% at 35 μmol L⁻¹, and 7% at the 190 μmol L⁻¹ level. The apparent N₂O concentration in the seawater was calculated according to the above equation. The highest N₂O concentrations of the headspace gas was around 2.5 ppm. The N₂O concentrations of the headspace gas fitted in our calibration curve.

3.3 Saturation ratio

The concentrations of the N₂O in the water samples were obtained from those that were measured in the headspace by subtracting the influence of atmospheric N₂O and using Bunsen coefficients to calculate the equilibrium solubilities, as described by Weiss and Price, (1980).

The atmospheric N₂O concentrations were taken from the NOAA/ESRL in situ program (http://www.esrl.noaa.gov/gmd). The annual average atmospheric N₂O concentrations at Mauna Loa
Saturation, expressed in %, was calculated using $R = \left( \frac{C_{\text{obs}}}{C_{\text{eq}}} \right)^{100}$ where $C_{\text{obs}}$ represents the observed concentration of the gas that was dissolved in the water, and $C_{\text{eq}}$ is the expected equilibrium water concentration, computed using the Henry’s Law.

3.4. Excess $N_2O$ ($\Delta N_2O$)

The excess $N_2O$ ($\Delta N_2O$) concentration was calculated as the difference between the calculated $N_2O$ equilibrium concentration and the observed $N_2O$ concentration as follows:

$$\Delta N_2O\left(\text{nmol} \cdot \text{L}^{-1}\right) = N_2O(\text{observed}) - N_2O(\text{equilibrium})$$

To calculate the $N_2O$ equilibrium concentration, different atmospheric mole fractions were used for different water layers. Between the mixed layer and the atmosphere, $N_2O$ exchanges occurred within three weeks or so (Najjar, 1992); thus, we calculated $N_2O$ in the mixed layer using the actual atmospheric $N_2O$ value. That is, the difference between the calculated $N_2O$ equilibrium concentration and the expected equilibrium concentration at depths of greater than 2000 m in the WPS was calculated using the tropospheric preindustrial value of 270 ppb (Fluckiger et al., 1999); for depths $> 2200$ m, an atmospheric value of 260 ppb (MacFarling Meure et al., 2006) was used.

Chen and Huang (1995), Chen et al. (2015) reported that waters in the SCS exchange rapidly and horizontally with the WPS so the intermediate and deep waters are essentially of the same age as corresponding waters in the WPS. The deep WPS water at around 2200 m flows across the deep sill (Chen et al., 2001) into the SCS and has become the deep water and the bottom water of the SCS (Nitani, 1972; Liu and Liu, 1988; Chen et al., 2001). Therefore, the waters at around 2200 m and deeper in the SCS are of similar age as the water at 2200 m in the WPS. Consequently, an atmospheric value of 270 ppb was used to calculate the $\Delta N_2O$ for the water depth greater than 350 m in the SCS.

### 3.5. Fluxes

Fluxes of $N_2O$ across the air-water interface were estimated using $F = k(C_w - \beta C_a)$ where $C_w$ represents the concentration of dissolved gas in the water (mol L$^{-1}$); $\beta$ is the Bunsen solubility, $C_a$ is the atmospheric gas concentration, and $k$ (cm h$^{-1}$) is the gas exchange coefficient. The value of $k$ is a specific function of the property of the gas, the temperature $T$ ($^\circ$C) and the wind speed $u$ (m s$^{-1}$). In the previous research, $k$ has commonly been calculated using the linear $k$/wind speed relationship that was established by Liss and Merlivat (1986) (LM86) or the quadratic $k$/wind speed relationship that was established by Wanninkhof (1992) (W92). Wanninkhof (2014) updated the frequently used method of Wanninkhof (1992), and a new $k$ was calculated. The updated relationship is given by $k = 0.251 u^2 (S/660)^{2.5}$, where $k$ is the gas transfer velocity; $u$ is the mean wind speed, and $S$ is the Schmidt number, which is the kinematic viscosity of water divided by the molecular diffusion coefficient of the gas. A positive flux indicates the gas transfer from the water to the atmosphere.

Wind speeds at 10 m above the surface were obtained from the National Aeronautics and Space Administration (NASA) QuikSCAT satellite platform (https://winds.jpl.nasa.gov/missions/quickscat). The average monthly wind speed was used to estimate the sea-to-air flux. The seawater fluxes from the SCS to the WPS were taken from Chen et al. (2001). The principle of conservation of water masses requires that the flow of water into the SCS be balanced by the outflow of water.

### 4. Results and discussion

#### 4.1. West Philippines Sea

The average surface $N_2O$ concentration in the WPS in the wet season was 5.19 $\pm$ 1.26 nmol L$^{-1}$ (90 $\pm$ 22% saturation; n = 43). In the WPS, the $N_2O$ (Fig. 2a) concentration gradually increased with the depth up to 1000 m, reaching a maximum of approximately 23 nmol L$^{-1}$ at 800–1000 m, coinciding with a DO minimum (Fig. 2b). The $N_2O$ concentration gradually decreased with depth beyond 1000 m because seawater at depths of greater than 1000 m in the WPS reflects the $N_2O$ distribution of the Pacific Deep Water (PDW), which has a low $N_2O$ concentration. According to Usui et al. (1998), Bange and Andreae (1999), the $N_2O$ concentration at depths of 3000–5000 m in the North Pacific is only around 17.5–22 nmol L$^{-1}$.

#### 4.2. South China Sea

The surface $N_2O$ concentration in the wet season in the SCS was 7.59 $\pm$ 1.32 nmol L$^{-1}$ (132 $\pm$ 23% saturation; n = 105). The $N_2O$
concentration in the water column of the SCS notably exceeds that in the WPS, and the SCS has a shallower N\textsubscript{2}O maximum (Fig. 3a) at approximately 600–800 m compared with the 800–1000 m in the WPS. This is due to the upwelling in the SCS. In both the SCS and the WPS, the N\textsubscript{2}O maxima (Figs. 2a and 3a) are at the depths where DO is at a minimum (Figs. 2b and 3b). The surface and intermediate waters are exchanged freely between the SCS and the WPS, and the deep water below 1350 m flows into the SCS from the WPS (Chen et al., 2001). However, waters at depths of greater than 2200 m in the WPS, including the Pacific Deep Water and the Antarctic Bottom Water, cannot enter the SCS (Chen et al., 2001, 2006). The intermediate and deep SCS waters above 2200 m mix with the WPS water, which has a lower N\textsubscript{2}O concentration, so the N\textsubscript{2}O concentration gradually decreases with increasing depth beyond the N\textsubscript{2}O maximum but remains constant at depths in excess of 2200 m.

In the SCS, some sampling stations close to the continental slope have high N\textsubscript{2}O concentrations (N\textsubscript{2}O > 32 nmol L\textsuperscript{-1}; Fig. 3a) at around 400–1000 m. Fig. 4 shows the cross-section in the northeastern SCS in 2003 (ORIII-896) and Fig. 5 presents the cross-section between the eastern and the southern SCS in 2007 (ORI-837). The water column of the sections were well stratified in both temperature and salinity in the summer (Figs. 4a, b, 5a, and b). The DO concentrations decreased from the surface layer to the DO minima (Figs. 4c and 5c) while N\textsubscript{2}O concentrations increased with the depth to the N\textsubscript{2}O maxima at approximately 600–800 m (Figs. 4d and 5d). Figs. 4d and 5d show that sampling stations close to the continental slope have high N\textsubscript{2}O concentrations at around 400–1000 m. Similarly, Zhang et al. (2008) measured high concentrations of N\textsubscript{2}O in the bottom waters of the continental slope in the East China Sea, which may have been related to the production and emission of N\textsubscript{2}O from the organic-rich sediments or re-suspended particles (Zhu et al., 2006). Lin et al. (1992) found a layer with a high particle concentration immediately above the sediments on the continental slope, probably as a result of the cross-shelf transport. Walsh et al. (1985) suggested that lateral particle transport in the water column has an important role in determining the final fate for the organic particle. Therefore, these high N\textsubscript{2}O concentrations are assumed herein to have been produced from organic particles on the continental slope close to the sampling stations. High CH\textsubscript{4} concentrations were also observed at the sampling stations close to the continental slope (Tseng et al., submitted).

4.3. Comparison of N\textsubscript{2}O distributions in the SCS and WPS

The average surface N\textsubscript{2}O concentration during the wet season in the SCS was about 30% higher than that in the WPS. There are many rivers flowing into the SCS, which discharge not only rich nutrients but also high concentrations of N\textsubscript{2}O (Chen et al., 2008). Fig. 6 presents the surface distribution of salinity and N\textsubscript{2}O near the Pearl River estuary in 2003. Higher N\textsubscript{2}O concentrations with lower salinities occurred near the estuaries (Fig. 6). This result indicates that the high surface N\textsubscript{2}O concentrations near the Pearl River estuary was caused by fresh water inputs. Additionally, upwelling often occurs in the SCS (Zheng and Tang, 2007; Han et al., 2013), bringing nutrients and high concentrations of N\textsubscript{2}O from greater depths to the surface waters. Furthermore, increasing nutrient contents and subsequent phytoplankton blooms (Zheng and Tang, 2007; Herbeck et al., 2011) may also influence the production and emission of N\textsubscript{2}O (Naik et al., 2008; Walker et al., 2010) in the SCS.

Figs. 2c and 3c show the distributions of NO\textsubscript{3}\textsuperscript{-} + NO\textsubscript{2}\textsuperscript{-} in the

![Graphs showing vertical distributions of N\textsubscript{2}O, DO, NO\textsubscript{3}\textsuperscript{-} + NO\textsubscript{2}\textsuperscript{-}, and ΔN\textsubscript{2}O in the West Philippines Sea.](image-url)
WPS and in the SCS, respectively. The NO$_3^-$/$C^0$ + NO$_2^-$/$C^0$ concentration at depths of less than 600 m in the SCS exceeds that in the WPS for two reasons. First, many rivers that are rich in NO$_3^-$/$C^0$ + NO$_2^-$/$C^0$ flow into the SCS. In particular, two of the largest rivers in the world (the Mekong and Pearl Rivers) enter from the north, contributing large amounts of nutrients and organic matter to the SCS, especially in the wet season (Yin et al., 2000; Chen et al., 2008). Also, the high-nutrient riverine water fuels higher productivity in the SCS relative to the WPS. Fig. 7 shows that the chlorophyll a concentrations in the surface and subsurface waters of the SCS are much higher than in the WPS, which reflects the higher productivity in the SCS.

Second, the deep WPS water flows across the deep sill (2200 m; Chen et al., 2001) into the SCS. This deep WPS water at around 2200 m becomes the deep water and the bottom water of the SCS (Nitani, 1972; Liu and Liu, 1988; Chen et al., 2001). The NO$_3^-$ + NO$_2^-$ accumulates in the SCS, because of the flow pattern. This effect, together with the vertical mixing and upwelling, brings NO$_3^-$ + NO$_2^-$ to the upper water, causing the concentration of NO$_3^-$ + NO$_2^-$ in the SCS to be higher than that in the WPS at depths of less than 600 m, but lower at depths of greater than 600 m.

The vertical profiles of N$_2$O and DO and, in particular, the coinciding N$_2$O maxima and DO minima (at 800–1000 m in the WPS and 600–800 m in the SCS), reveal that nitrification dominates the N$_2$O production, as was also found in previous research (Yoshinari, 1976). In short, the SCS has shallower N$_2$O maxima and DO minima than the WPS because of the intensive upwelling.

4.4. In situ biological production

Most studies in the field have used the contemporary atmospheric N$_2$O mole fraction, which is independent of the “real” age of the sampled water masses for the calculation of ΔN$_2$O. This approach is highly suitable for calculating ΔN$_2$O in waters in surface layers, but neglects the effect of the age of the water mass and, therefore, the variable atmospheric mole fraction that is involved in establishing an initial “equilibrium” (Walter et al., 2006; Freing et al., 2009). Nevison et al. (2003) asserted that the use of only the contemporary atmospheric mole fraction introduces an uncertainty of 10–15% in the estimate of ΔN$_2$O. Walter et al. (2006) showed that using “the contemporary atmospheric mole fraction” instead of “the initial atmospheric mole fraction” yielded a 7% smaller ΔN$_2$O at depths of less than 2000 m, and a 17% smaller ΔN$_2$O at depths of greater than 2000 m in the North Atlantic Ocean. This ΔN$_2$O difference at a particular depth may be higher in the Pacific Ocean than in the Atlantic Ocean because the deep water masses in the Pacific Ocean are older (England, 1995; Gebbie and Huybers, 2012). Fig. 8 presents the effect of depth-dependent initial atmospheric mole fractions on the ΔN$_2$O. There is no difference between the results above 350 m because the initial atmospheric mole fraction is taken to be equal to the contemporary atmospheric mole fraction. On the other hand, the equilibrium concentration of N$_2$O below 350 m is generally lower than those obtained using a uniform N$_2$O mole fraction because “the initial atmospheric N$_2$O mole fraction” is lower than “the contemporary atmospheric N$_2$O mole fraction.” Thus, the ΔN$_2$O may be underestimated by using a uniform atmospheric N$_2$O mole fraction. Therefore, we calculated the ΔN$_2$O herein by using different atmospheric N$_2$O.
mole fractions for different water layers to reduce the uncertainty of the $\Delta$N$_2$O. Note there is a discontinuity in the percentage deviation of $\Delta$N$_2$O at 350 m. This is caused by the sudden change of the initial atmospheric mole fraction from 318 to 321 ppb for waters above 350 m to 270 ppb for waters below 350 m. This artifact cannot yet be resolved without the knowledge of the exact age and the corresponding atmospheric N$_2$O concentration for subsurface water masses.

The $\Delta$N$_2$O deviations at around 400–600 m in the WPS are rather large, because waters there have lower N$_2$O concentrations compared with that in the deeper water. To calculate $\Delta$N$_2$O by using “the contemporary atmospheric mole fraction” instead of “the initial atmospheric mole fraction” may cause an error as high as 19% of the $\Delta$N$_2$O deviation, especially in the area where has low N$_2$O concentrations. The mean $\Delta$N$_2$O deviation below the surface layer is about $-6.1 \pm 2.0\%$ (n=131) in the WPS and $-4.1 \pm 0.5\%$.
Several investigations have reported linear relationships between ΔN₂O and AOU in various oceanic areas (Yoshinari, 1976; Elkins et al., 1978; Cohen and Gordon, 1979; Butler et al., 1989; Law and Owens, 1990; Oudot et al., 1990; Naqvi and Noronha, 1991; Naqvi et al., 1994; Nevison et al., 1995, 2003). The AOU quantifies the amount of O₂ that is consumed by the remineralization of organic matter and nitrification in a water parcel since its last contact with the atmosphere. A strong correlation between AOU and ΔN₂O in the oceans is frequently observed, providing circumstantial evidence that nitrification is the dominant mechanism of oceanic N₂O production (Yoshinari, 1976; Elkins et al., 1978; Cohen and Gordon, 1979; Butler et al., 1989; Patra et al., 1999; Nevison et al., 2003).
and NO$_3^-$ concentration, ΔAOU (Fig. 10a) and between August 2003 and July 2007. Philippines Sea above depth of 500 m, obtained at 91 stations during six cruises between August 2003 and July 2007. The relationships between ΔN$_2$O and AOU and ΔN$_2$O and NO$_3^-$ are studied to provide further insight into the biological production of N$_2$O. Horrigan et al. (1981) indicated that the production of N$_2$O is insignificant in the euphotic zone (from the surface to a depth of 15–100 m), where denitrifiers are inhibited by high oxygen concentrations and nitrifiers are inhibited by light and low NH$_4^+$ availability. To exclude the effects of sea-air exchange and photo-inhibition, the correlations between ΔN$_2$O and AOU (Fig. 10a) and between ΔN$_2$O and NO$_3^-$ (Fig. 10b) from the lower euphotic zones (around 100 m) to the depth of the maximum N$_2$O concentration were examined. The ΔN$_2$O correlates positively with AOU (WPS: ΔN$_2$O=0.091AOU-0.33, n=111, $r^2=0.96; \text{SCS: } \Delta N_2O=0.121AOU-0.17; \quad n=179, \quad r^2=0.87)$ and NO$_3^-$ (WPS: ΔN$_2$O=0.53[NO$_3^-$]+0.60, n=111, $r^2=0.94; \text{SCS: } \Delta N_2O=0.70[NO_3^-]+2.86, \quad n=179, \quad r^2=0.88)$, suggesting that nitrification is the major mechanism of the N$_2$O production at depths of less than 1000 m in the WPS and 800 m in the SCS. The slopes of the linear correlations between ΔN$_2$O and AOU provide estimates of the amount of N$_2$O that is generated per amount of DO consumed (Nevison et al., 2003; Walker et al., 2010). N$_2$O yields from nitrification can be estimated from the DO consumption per mole of N$_2$O produced (Grundle et al., 2012), following the Redfield stoichiometry (Redfield et al., 1963), which attributes approximately 17.3% of the total DO consumption to the NH$_4^+$ oxidation (Ward, 2008). The correlations of ΔN$_2$O with AOU were utilized herein to reveal that the N$_2$O yield from nitrification was 0.053±0.001% in the WPS and 0.070±0.002% in the SCS between a depth of 100 m and that of the maximum N$_2$O concentration. Strong correlations between NO$_3^-$ and AOU (Fig. 11c; WPS: [NO$_3^-$]=0.168[AOU]−1.43, n=111, $r^2=0.98; \text{SCS: } [NO_3^-]=0.167[AOU]−2.81, \quad n=179, \quad r^2=0.91)$ were also found, owing to nitrification in both the WPS and the SCS, as were also found in the western North Pacific (Yoshida et al., 1989). Hence, N$_2$O yields of nitrification could be estimated directly from the molar ratio of N$_2$O production to NO$_3^-$ production, which was 0.053±0.001% for the WPS and 0.070±0.002% for the SCS from a depth of 100 m to the depth of the maximum N$_2$O concentration. These estimates match exactly those estimated from the relationship of ΔN$_2$O versus AOU. This finding supports that most of the N$_2$O in the subsurface water in the WPS and the SCS is produced by nitrification.

N$_2$O yield from nitrification in the SCS herein slightly exceeded 0.065% in the shelf region of the SCS (Han et al., 2013), and was also higher than the WPS. N$_2$O yields of nitrification in both the SCS and the WPS are higher than those reported elsewhere for the North Pacific Ocean (range, 0.004–0.027%; Yoshida et al., 1989), the NE subarctic Pacific Ocean (range, 0.028–0.040%; Grundle et al., 2012), and the subtropical Atlantic Ocean (0.030–0.040%; Walter...
et al., 2006), but are similar to those obtained for the tropical Atlantic Ocean (0.06–0.08%; Walter et al., 2006).

At depths greater than that of the maximum $N_2O$ concentration, the linear relationships between $\Delta N_2O$ and AOU (Fig. 11a) as well as $\Delta N_2O$ and $NO_3^-/C_0$ (Fig. 11b) in both the SCS and the WPS are statistically insignificant, presumably owing to changing $N_2O$ yields and/or physical mixing of different water masses. Fig. 12 shows that the $\Delta N_2O/AOU$ ratios decrease with depth but remain constant below 1000 m both in the SCS and the WPS. Butler et al. (1989) hypothesized that the decline in the $N_2O$ concentration with depth may reflect the pressure inhibition of the primary nitrification pathway that leads to the $N_2O$ production. Nevison et al. (2003) and Codispoti (2010) also pointed out that the $N_2O$ concentration and the $\Delta N_2O/AOU$ ratio tend to decrease at high pressure or AOU. The $\Delta N_2O$ concentrations and $N_2O$ yields that are presented herein represent the $N_2O$ production over the history of the water mass, rather than simply showing localized in situ production; since, the concentrations of preformed $N_2O$ and the effects of conservative mixing were not eliminated (Nevison et al., 2003; Grundle et al., 2012).

In the WPS, the mean of the $\Delta N_2O/AOU$ ratio below the $N_2O$ maximum (800–1000 m) was $0.071 \pm 0.008$ ($n=49$), while the mean $\Delta N_2O/AOU$ ratio above the $N_2O$ maximum was $0.091 \pm 0.016$ ($n=86$). In the SCS, the mean of the $\Delta N_2O/AOU$ ratio below the $N_2O$ maximum (600–800 m) was $0.096 \pm 0.013$ ($n=109$), while the mean $\Delta N_2O/AOU$ ratio above the $N_2O$ maximum was $0.118 \pm 0.019$ ($n=180$). In all, biological $N_2O$ production per mole DO consumed in the SCS was around 23–26% higher than that in the WPS. This explains why $N_2O$ distributions in the SCS were about 20% higher than that in the WPS.

The $\Delta N_2O/AOU$ ratios decreased at depths greater than that of the maximum $N_2O$ concentration in the SCS, maybe because high pressure inhibited the primary nitrification pathway (Butler et al., 1989). However, since DO concentrations in the SCS deep water were at a relatively high level of around 100 $\mu$mol L$^{-1}$,
denitrification did not occur there. The N$_2$O concentrations decreased below the depth of the N$_2$O maximum in the SCS due to mixing with the WPS deep water, which has low N$_2$O concentrations. The N$_2$O concentration maximum in the SCS was about 28.85 nmol L$^{-1}$ and the salinity was around 34.46 (Fig. 13) at depth of around 600–800 m. The N$_2$O concentration of the deep water layer (1350–2200 m) in the WPS was 20.43 nmol L$^{-1}$ and the salinity was 34.62. The WPS deep water flows into the SCS and mixes with the WPS intermediate water, then becomes the SCS deep water with a salinity of 34.60. Calculation based on salinity indicates that the deep water of the SCS is composed of 88% WPS deep water and 12% SCS water at the N$_2$O maximum (0.88 × 34.62 + 0.12 × 34.46 = 34.60). According to the water masses mixing ratio, 21.39 nmol L$^{-1}$ of the N$_2$O concentration in the SCS deep water should have come from physical mixing (0.88 × 20.37 + 0.12 × 28.85 = 21.39). As a result, 85% of the N$_2$O concentration in the SCS deep water was from physical mixing and 15% was from biological N$_2$O production.

4.5. Air-sea N$_2$O exchange

During the wet season, the mean surface N$_2$O in the SCS was oversaturated and the sea-to-air flux was 5.5 ± 3.9 μmol m$^{-2}$ d$^{-1}$ (Table 2). The mean N$_2$O flux in the SCS during the wet season herein exceeds those from the shelf area of northwestern SCS (1.7 ± 1.6 μmol m$^{-2}$ d$^{-1}$; Han et al., 2013) and those from the southern Baltic Sea (2.3–4.0 μmol m$^{-2}$ d$^{-1}$; Bange et al., 1998). However, the flux in the SCS is comparable with or is only slightly lower than those from other seas – such as 9.8–17.1 μmol m$^{-2}$ d$^{-1}$ from the East China Sea (Zhang et al., 2008); 4.7–8.4 μmol m$^{-2}$ d$^{-1}$ from the North Yellow Sea (Yang et al., 2009); 5.2 μmol m$^{-2}$ d$^{-1}$ from the northwestern Black Sea (Amouroux et al., 2002), and 6.8–11.9 μmol m$^{-2}$ d$^{-1}$ from the north-eastern shelf of the Gulf of Cadiz (Ferrón et al., 2010). The SCS contributes about 0.1 Tg N to the atmosphere in the wet season which lasts for six months.

The mean surface N$_2$O concentration in the WPS in the wet season was undersaturated and the sea-to-air flux was −1.7 ± 3.9 μmol m$^{-2}$ d$^{-1}$ (Table 2). The WPS, the Golfe du Lion (Marty et al., 2001) and the Adriatic Sea (Leip, 1999) are a few of the marine areas for which N$_2$O undersaturations have been reported upon (Bange, 2006).

### Table 2

Compilation of N$_2$O measurements in various coastal, shelf and marginal seas.

<table>
<thead>
<tr>
<th>Study area</th>
<th>Date</th>
<th>Surface N$_2$O (nmol L$^{-1}$)</th>
<th>Saturation (%)</th>
<th>Sea-to-Air Flux (μmol m$^{-2}$ d$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW Black Sea</td>
<td>Jul.–Aug. 1995</td>
<td>8.0 ± 0.8</td>
<td>110</td>
<td>3.1; 5.2a</td>
<td>Amouroux et al., 2002</td>
</tr>
<tr>
<td>Caribbean Sea</td>
<td>June 1996</td>
<td>7.14 ± 0.21</td>
<td>120 ± 4</td>
<td>0.014 ± 0.014c</td>
<td>Morell et al., 2001</td>
</tr>
<tr>
<td>Arabian Sea</td>
<td>Apr. 1995</td>
<td>6.60 ± 0.55</td>
<td>114 ± 9</td>
<td>0.069 ± 0.070c</td>
<td></td>
</tr>
<tr>
<td>Southern Baltic Sea</td>
<td>June 1994–Apr. 1997</td>
<td>123</td>
<td>103–107</td>
<td>0.35–3.9%</td>
<td>Bange et al., 1996b</td>
</tr>
<tr>
<td>Aegean Sea</td>
<td>July 1993</td>
<td>7.02–7.27</td>
<td></td>
<td>1.2–21.0a</td>
<td>Bange et al., 1996b</td>
</tr>
<tr>
<td>Central North Sea and German Bight</td>
<td>Sep. 1991</td>
<td>8.4–9.2</td>
<td>99–104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>West Bay of Bengal</td>
<td>Mar.–Apr. 1991</td>
<td>125.2 (89.3–214)</td>
<td>107 ± 3</td>
<td>0.65% (–1.0–10.7)</td>
<td>Naqvi et al., 1994</td>
</tr>
<tr>
<td>Eastern Ionian Sea</td>
<td>Jul 1993</td>
<td>86 (0–197)</td>
<td>171 (84–309)</td>
<td></td>
<td>Bange et al., 1996a</td>
</tr>
<tr>
<td>Gulf of Lions (Mediterranean Sea)</td>
<td>Jun 1998</td>
<td>93 (85–100)</td>
<td></td>
<td></td>
<td>Marty et al., 2001</td>
</tr>
<tr>
<td>Gulf of Thermaikos</td>
<td>Apr 1998</td>
<td>93 (85–100)</td>
<td>93 (85–100)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adriatic Sea</td>
<td>Aug 1996</td>
<td>93 (85–100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NE shelf of the Gulf of Cadiz</td>
<td>Jun, Nov. 2006; Feb, May 2007</td>
<td>9.4–19.5</td>
<td>120–255</td>
<td>6.8 ± 6.4%; 11.9 ± 10.6%</td>
<td>Ferrón et al., 2010</td>
</tr>
<tr>
<td>North Yellow Sea</td>
<td>Mar. 2005; Apr., Aug. 2006; Apr., Oct. 2007</td>
<td>12.0</td>
<td>4.7 ± 6.8%</td>
<td></td>
<td>Yang et al., 2009</td>
</tr>
<tr>
<td>East China Sea</td>
<td>Sep. 2003</td>
<td>11.5 ± 4.5 (5.75–241)</td>
<td>191 ± 74 (94–382)</td>
<td>9.8 ± 16.0%; 17.1 ± 26.4%</td>
<td>Zhang et al., 2008</td>
</tr>
<tr>
<td>West Philippines Sea</td>
<td>Aug. 2004; May 2006; Jul. 2007</td>
<td>5.19 ± 1.26</td>
<td>90 ± 22</td>
<td>−1.7 ± 3.9%</td>
<td>This study</td>
</tr>
<tr>
<td>Northwestern South China Sea</td>
<td>Aug. 2008</td>
<td>5.51–7.74</td>
<td>99–123</td>
<td>1.1 ± 10%; 1.7 ± 16%</td>
<td>Han et al., 2013</td>
</tr>
<tr>
<td>South China Sea</td>
<td>Aug., Sept. 2003; Jul. 2004; Jul. 2006; Jul. 2007</td>
<td>7.59 ± 1.32</td>
<td>132 ± 23</td>
<td>5.5 ± 3%</td>
<td>This study</td>
</tr>
</tbody>
</table>

Flux estimations are follows:

a Liss and Merlivat (1986);
b Wanninkhof (1992);
* Wanninkhof (2014).
Positive and negative numbers represent inflow and outflow, respectively.

4.6. Water mass and N₂O exchange between the SCS and the WPS

During the wet season, a net export of surface and intermediate waters from the SCS to the WPS occurs but there is a net import of deep water (Chen et al., 2001). The N₂O concentration at depths less than 350 m in the SCS (the SCS surface water layer) was 11.23 ± 5.17 nmol L⁻¹; that in the WPS (the WPS surface water layer) was 6.52 ± 2.82 nmol L⁻¹ (Table 3). Chen et al. (2001) calculated the flow of surface water out of the SCS through the Bashi Channel during the wet season at 13.9 × 10⁸ t s⁻¹, and the flow of WPS into the SCS at 12.8 × 10⁸ t s⁻¹. Overall, the net exports of surface water from the SCS to the WPS carries 6.3 × 10⁸ mol d⁻¹ N₂O during the wet season.

The SCS intermediate water, as defined by Chen and Huang (1996) based on observational data, is at depths of between 350 and 1350 m, and is a mixture of the upwelled deep water and the surface water. The intermediate water flows out of the SCS at a rate of 1.8 × 10⁸ t s⁻¹ (Chao et al., 1996; Chen and Huang, 1996) with an N₂O concentration of 27.49 ± 2.88 nmol L⁻¹. Thus, the SCS intermediate water exports 4.3 × 10⁸ mol d⁻¹ N₂O to the WPS.

The deep water at depths of greater than 1350 m flows into the SCS year-round at a rate of 1.2 × 10⁸ t s⁻¹ (Chao et al., 1996; Chen and Huang, 1996). Since the deepest sill that connects the SCS with the WPS is 2200 m deep, water that is deeper than 2200 m cannot enter the SCS. The N₂O concentration of the deep water layer (1350–2200 m) in the WPS was 20.37 ± 1.84 nmol L⁻¹, so the deep water from the WPS exports 2.1 × 10⁸ mol d⁻¹ N₂O to the SCS.

Overall, in the wet season, the SCS exports 8.5 × 10⁸ mol d⁻¹ N₂O (net value) to the WPS and emits 19.3 × 10⁸ mol d⁻¹ N₂O to the atmosphere; and the SCS exports a larger amount of N₂O to the atmosphere than it transports to the WPS.

5. Conclusions

The surface waters are oversaturated in N₂O with respect to the atmosphere in the SCS, and undersaturated in the WPS. During the wet season, the SCS is a source of atmospheric N₂O at a rate of 5.5 ± 3.9 μmol m⁻² d⁻¹, and the WPS is a sink of atmospheric N₂O at a rate of −1.7 ± 3.9 μmol m⁻² d⁻¹.

The N₂O concentration in the water column in the SCS is higher than that in the WPS. The N₂O concentration in the WPS reached a maximum at a depth of 800–1000 m; the corresponding depth in the SCS was only around 600–800 m, owing to vertical mixing and intensive upwelling. Excess N₂O correlates positively with AOU and NO₃⁻ suggesting that nitrification is the major mechanism of N₂O production at depths of less than 1000 m in the WPS and 800 m in the SCS. The N₂O yield from nitrification was 0.053% in the WPS and 0.070% in the SCS between a depth of 100 m and that of the maximum N₂O concentration, based on correlations of excess N₂O versus AOU and NO₃⁻ concentrations. This study has established that the SCS emits N₂O to the atmosphere and exports N₂O to the WPS.

Acknowledgements

The authors wish to thank the Ministry of Science and Technology of the ROC, Taiwan (MOST 104–2611–M–110–015 and 104–2611–M–110–016) and the Aim for the Top University Program Project (04C030204 and 05C030204), for supporting this research, and the captains and crews of ORI and III for their assistance. This work was also supported by the Erasmus Mundus Joint Doctorates program in Marine and Coastal Management under the UNESCO/UNITWIN/WiCop research and academic activities. AVB is a senior research associate at the Fonds National de la Recherche Scientifique (FNRS, Belgium). Three anonymous reviewers provided constructive comments which helped strengthening the manuscript.

References


