CHARACTERISTICS OF N_2O DISTRIBUTIONS AT AIR-SEA INTERFACE ON THE EQUATOR AREA IN PACIFIC OCEAN

Masahiro Imamura[1], Nobuhito Mori[2],
Kiminori Shitashima[1] and Ryousuke Yamamoto[1]

Abstract

The N_2O concentration on the equator area in Pacific Ocean from sea surface to deep water at January 1999 and December 1999 was observed. In the series of cruises, observed N_2O near the sea surface was about less than 10nM and the maximum value was 40-50nM in depth of 200-800m. The surface N_2O saturation values (SN_2O) ranged from 30 to 110%. Variations in the SN_2O near the sea surface are caused mainly by the sea metrology (such as wind speed and wave height). The correlation coefficient between significant wave height and SN_2O is significantly higher than that value between the wind speed and SN_2O.

KEYWORDS: *N_2O, equator area, gas solubility, wind speed, wave height*

1. Introduction

N_2O gas is one of greenhouse effect gasses on the earth and it remains very long period in the atmosphere. Thus, it contributes to global warming and ozone depletion. Ocean is unknown about sink and source area of greenhouse gasses on the earth. The only significant sink of N_2O is photo-dissociation and photo oxidation in the stratosphere. The total N_2O source strength has been estimated in between 15.7 and 26.7 Tg-N year^{-1} (Houghton *et al.* 1992).

The one of major sink and source of N_2O gas was considered as the ocean. However, it's not dominant for the total balance of income and expenditure on the earth (*e.g.* Khalil and Rasmussen 1992, Bouwman *et al.* 1995). The atmospheric N_2O was 275ppbV before the industrial revolution and increased to 310–340ppbV at the present time. N_2O gas is generally produced by biological reaction in sediments and combustion of biomass. The N_2O is produced in seawater as byproduct of both nitrification and denitrificaiton processes (Yoshinari 1976, Yoshida *et al.* 1989). Nitrification, which is believed to be the major contributor to the production of N_2O in seawater, has a yield equivalent to only 0.1% of moles O_2 consumed during the conversion from NH_4^+ to NO_3^- (Najjar 1992). However, in anoxic waters the processes of denitrification consume N_2O (Cohen and Gordon 1978, Mantoura *et*

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[1] Department of Environmental Science, Central Research Institute of Electric Power Industry (CRIEPI), 1646 Abiko, Abiko, Chiba 270-1194, Japan

[2] Department of Fluid Mechanics, Central Research Institute of Electric Power Industry (CRIEPI) , 1646 Abiko, Abiko, Chiba 270-1194, Japan

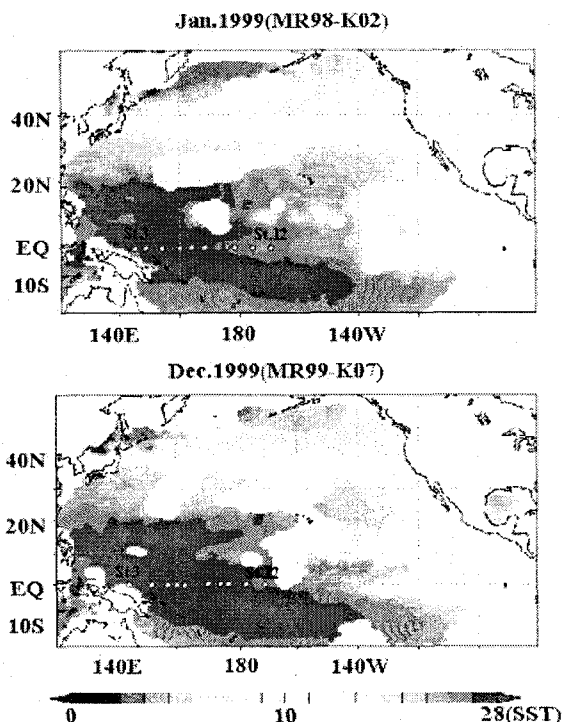Jan.1999(MR98-K02)

Dec.1999(MR99-K07)

Figure 1. Locations of sampling stations and corresponding sea surface temperature of two cruises (top figure: MR98-K02, bottom figure: MR99-K07, original figures are provide by NOAA)

al. 1993).

The air-sea interface is very important to connect gas circulation cycle of carbon and nitrogen on the earth. However, the detail of distributions in the ocean of the greenhouse gasses is not clarified. Estimation of gas flux at the air-sea interface is very important because it is boundary condition for earth climate simulations. Therefore, sea-surface conditions, seawater chemical conditions and gas chemical conditions effect on gas transfer velocity at the air-sea interface. Thus, many studies have been made the gas exchange at the air-sea interface. For example, the CO_2 gas exchange rate increases with quadric curve as a function of sea surface wind speed more than 10m/s, although it increases linearly for low speed wind (Liss 1997). Liss and Merlivant (1986) and Wanninkhof (1992) were investigated the effects of the air-sea interface models on the total gas exchange of global climate model. They estimated CO_2 cycle on the earth with the different air-sea interface boundary models. The estimated rates were several times different among them (Peng 1990). Thus, it is necessary to measure and verify the conditions at the air-sea interface. Recently, many greenhouse gas potentials on the ocean surface are observed (*e.g.* Weiss *et al.* 1992), although the most of observations related with N_2O were conducted at North Pacific and Indian Oceans (Pierotti and Rasmussen 1980, Poisson *et al.* 1993).

In this study, we report the detail of spatial and vertical distributions of N_2O from deep-sea to sea surface water on the equator area in the Pacific Ocean at January 1999 and December 1999. The objectives of this study are 1) to investigate the N_2O distribution on the equatorial area in the Pacific Ocean, and 2) to indicate the relationship among surface water N_2O enrichment and local sea states, such as sea surface wind speed, wave height, water temperature and gas concentration by observational data.

2.   Observation Area and Locations of Sampling Stations

Measurements of dissolve and atmospheric N_2O and etc were performed on board of the formed Japanese research vessel *R.V. MIRAI*, during a cruise from Guam to Honolulu, January 1999 (cruise name: MR98-K02) and December 1999 (cruise name: MR99-K07). The measurements were made within Japan Marine Science and Technology Center (JAMSTEC) conducted bio-chemical observation cruise on the Pacific equator area. Cruise tracks are illustrated in **Fig.1**. Continuous measurements of surface seawater and meteorological measurements were made through the cruises. We made hydro-casts at 12 stations for each cruises.

3.   Method of Analysis and Materials

Samples for N_2O analysis were drawn from the Niskin samplers into 125ml glass vial bottles after an overflow of about 100ml of the seawater. The samples were immediately poisoned with 50µl of 50% saturated $HgCl_2$ in order to restrict biological alteration prior to sealing the bottles. All samples were stored in a refrigerator before analysis and were analyzed within 12 hours after collection.

The concentration of N_2O was determined using a headspace method. About 15ml of headspace N_2 gas was introduced into a glass vial bottle by removing seawater with syringe. Subsequently, the samples were standing in thermostatic water bath (40 ± 0.5°C) for at least 2 hours in order to make a gas-liquid equilibration. The N_2O in headspace gas was took with a gas syringe and injected to gas chromatograph with [63]Ni electron capture detector (equipment: ECD-GC14 Shimazu on board, column: molecular sieve 5A 60/80*2m, column temp: 200°C, inj/det temp:300°C, flow rate of carrier gas:20ml/min).

Saturation of gas were calculated as the ratio of the concentration of dissolved gas and the expected equilibrium water concentration of the gas, derived from the ambient air dry mole fraction:

$$Sat = 100 \times (C_W / C_a) \qquad (1)$$

where $C_W = \beta X_{equi}$, $C_a = \beta X_{atms}$, β is the Bunsen solubility for N_2O, X_{equi} is the measured dry mole fraction of N_2O in the headspace of the equilibration and X_{atms} is the measured dry mole fraction of N_2O in atmosphere. The concentration of dissolved N_2O in the seawater was calculated with the fractions for the solubility given by Weiss and Price (1980). Saturation values (SN_2O) were calculated as the ratio of the expected saturation concentration of N_2O and its measured concentration in the seawater. On the other hand, sea surface temperature (SST), humidity, wind speed U_{10}, significant wave height $H_{1/3}$ and period $T_{1/3}$ were continuously measured using ship mounted sensor and ultra sonic wind and wave gages.
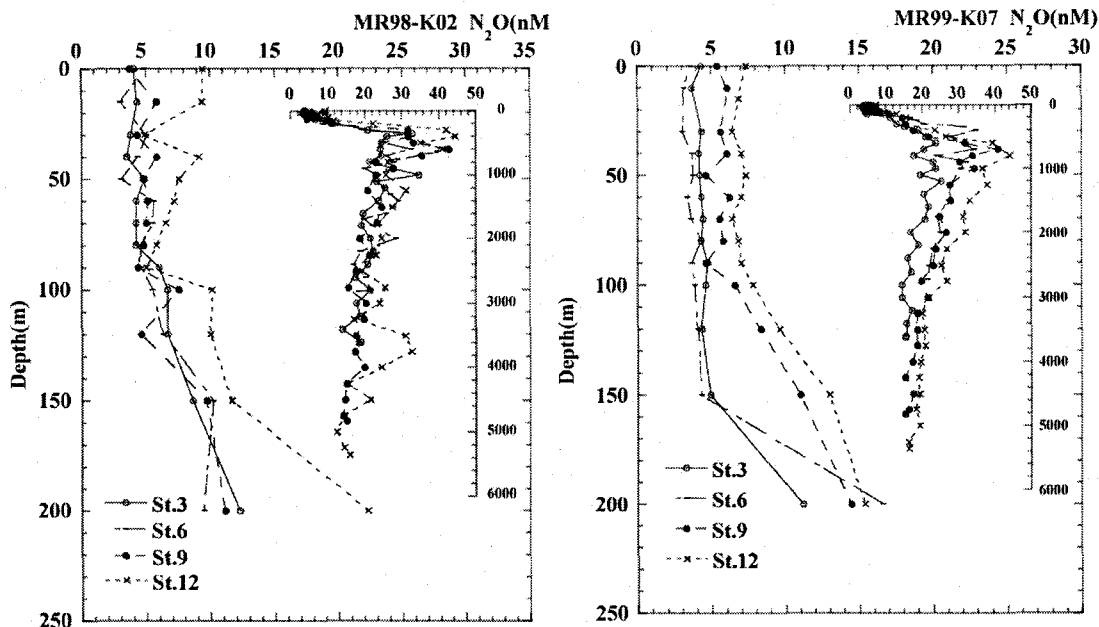
Figure 2. Vertical distribution of N_2O at Jan. 1999 (MR99-K02) and Dec.1999 (MR99-K07)

4.   Results and Discussion

4.1 N_2O distribution in water column

The profiles of vertical distributions of N_2O concentration at January 1999 (MR98-K02) and December 1999 (MR99-K07) are shown in **Fig.2 and 3**. The mean values of N_2O concentration at the sea surface (0-10m) were 4-9nM. It corresponds to 30-110% of fully saturated value. The maximum values of N_2O concentration in the water column were 40-50nM. It also corresponds to 300-600% of fully saturated value at individual water depth around 200-800m. Only at St.12, the N_2O concentration in water column were the higher than that of concentration at other station. The reason why the only St.12 had very high concentration value is that the equatorial area on the Pacific Ocean was shifted from El Niño to La Niña at this location St.12, early 1999. In addition, a temperature decreasing at the surface seawater was observed at the end of east side area on the Pacific Ocean at the same time. Moreover, upwelling nutrient current from the lower layer was also observed and it supported to this sea state (JAMSTEC 1999). Therefore, it is clear that upwelling of cold N_2O-rich water was the dominant source of N_2O in the low layer (St.9, 12). N_2O concentration on the sea surface shows lower tendency in MR99-K07 than MR98-K02. But the N_2O concentration increased only in the area between St.9 and St.12 of MR99-K07 (0-100m deep). The influence of the high nutrient concentration water transfer from the middle layer to the sea surface was observed at St.9 (180°E). The production of biological N_2O according to this nutrient upwelling was N_2O increase
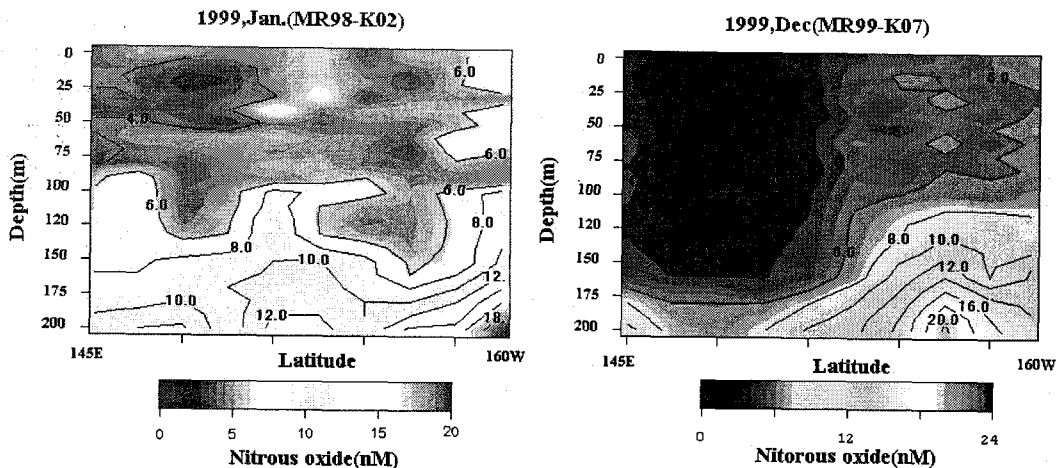
Figure 3. Distribution of N$_2$O on the equator in the Pacific Ocean at Jan. 1999
(MR99-K02) and Dec.1999 (MR99-K07)

cause in the area between St.9 and St.12 of MR99-K07.

Some N$_2$O concentrations were low in equatorial waters over all layers compared with other sea areas (Hashimoto *et al.* 1998, Hein *et al.* 1997, and Prabir *et al.* 1999) but the concentration distribution characteristic in a perpendicular direction showed almost the same tendency. As for equatorial waters, the nutrient concentration is thought that it is one of factors that the concentration lowers that low regret and the temperature of the surface seawater are 30°C and are high compared with other points.

4.2 Meteorological condition

The atmospheric and sea conditions during observations at MR98-K02 and MR99-K07 are shown in **Fig.4**. Both of the observation periods, wind speed was relatively constant round 6-8m/s. Relationship between the wind speed and the wave height has high correlation coefficient, but in the case of low wind speed less than 4m/s, the correlation between the wind speed and the wave height becomes lower. It is because effects of swell. Generally, the gas exchange at the air-sea interface is formulated the gas transfer velocity as a function of sea surface wind (*e.g.* Liss and Merlivant 1986). But there were many conditions to influence the gas transfer velocity near the sea surface such as gas solubility, breaking wave induced air bubbles, white caps and so on.

Solubility of N$_2$O gas in seawater depends on water temperature and salinity. In the MR98-K02 cruise, equate surface water temperature were immediately low degree from 160°E. Reason for that, La Niña condition was in this time spring 1999. La Niña is characterized by unusually cold ocean temperatures in the Equatorial Pacific, so that, nutrient concentration were increasing as east area by
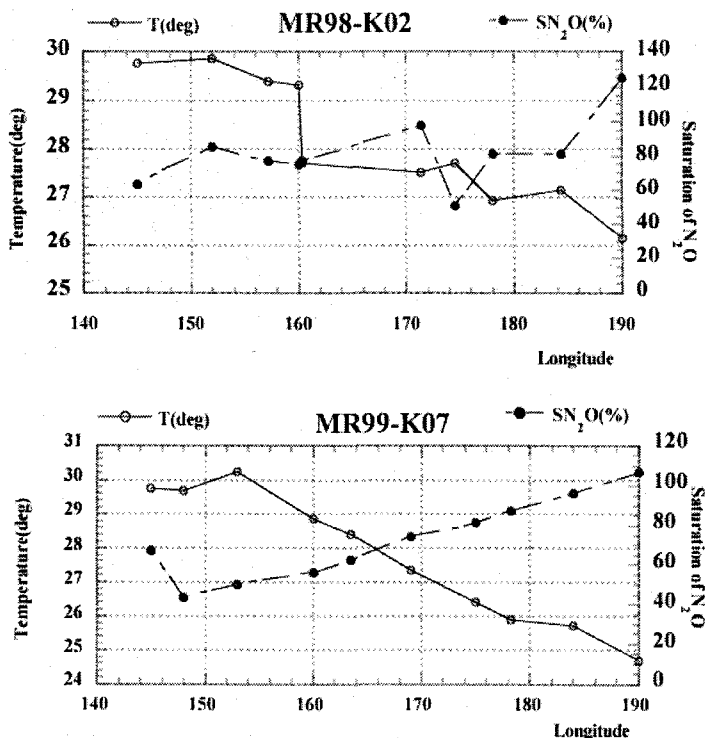
Figure 4. Changing of surface seawater temperature and saturation of N_2O rate
on equator in the Pacific Ocean.

upwelling deep water. Saturation rate of N_2O in sea surface was relationship of water temperature. Liss and Merlivant (1986) and Jahne (1990) experimentally investigated the gas transfer velocity dependence on the sea surface wind with high accuracy. The gas exchange of N_2O cannot be estimated by their observations, because Schmit number Sc and solubility of N_2O are different from CO_2. During the series of observations, we didn't measure the gas transfer velocity, because we didn't measure twice at the same location. However, it is able to consider bulk variations of gas saturation, and atmospheric and sea state.

Atmospheric and sea state can be roughly estimated by the average sea surface wind velocity and significant wave height $H_{1/3}$ just before several hours of water sampling. The temporal variations of sea surface wind speed and wave height are shown in **Fig.5**. The wave height in MR99-K07 was higher then MR98-K02 while the velocity of the sea surface wind was almost equal at St.12, the west end. The water temperature of MR99-K07 at the same point (St.12) was lower than MR98-K02, but N_2O saturation of MR99-K07 is lower than that of MR98-K02. It is thought that the external factor by the wave breaking joins the sea surface.

In addition, there is no big difference of the sea surface temperature between MR98-K02 and MR99-K07, although SN_2O was decreased in the vicinity of St.4 (150°E) of MR99-K07. It is interested that the small-scale wave breaking was visually observed at the sea surface, even if the velocity of the wind was slow.
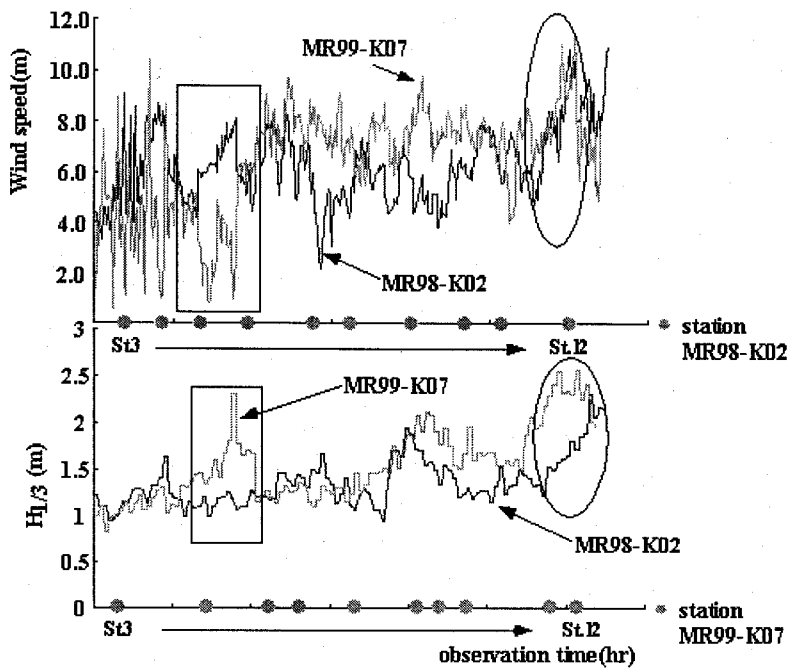
Figure 5. Average velocity of the wind when observing it and observation of significant wave high ($H_{1/3}$)

4.3 Production and Distribution of N_2O in Deep-Sea

In the central Pacific Ocean, the major contribution of nitrogen cycle is phytoplankton organic matter. Production of N_2O in the seawater depends on the biochemical reaction (Yoshinari 1976). Generally, as decreasing concentration of dissolve oxygen for vertical direction, the nitrification activity is the gradually decrease (*e.g.* Yoshinari 1976, Elkins *et al.* 1978). As the results, N_2O is produced as the middle production for nitrification (Devol, 1978).N_2O at all stations shows negative correlation between O_2 (50-100µmol/kg at maximum layer of N_2O) and shows positive correlation between NO_3^- (20-30µmol/l at maximum layer of N_2O). These relationships can be observed typically around the Worlds Ocean, and it is consistent with N_2O production by nitrification (Yoshinari 1976). The dissolved oxygen was decrease about 100-500m in both cases, it means that denitrification reaction was increased in this depth. Thus, it can be considered that the reaction of nitrification and denitrification were active in this layer (100-500m).

Spatial variation of N_2O concentration in the direction of longitude was greatly changed due to the amount of nutrient supply. It is mainly due to variation of water temperature and salinity, although the explanation of variation of N_2O saturation due to water temperature and salinity alone are too
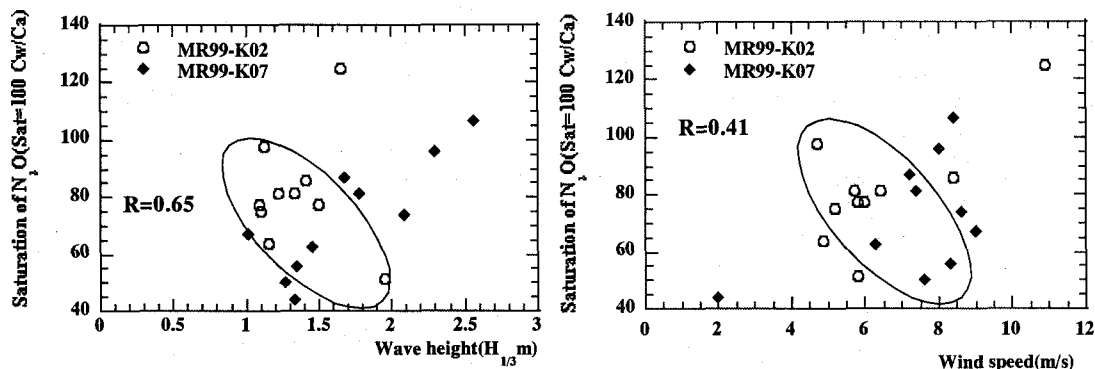
Figure 6. Relation of the saturation values (SN_2O) for the average velocity
of the wind and the significant wave height

simple. In the shallow water layer from surface to about depths of 100m, N_2O concentration was changed drastically, but it was scatter near the sea surface below 5-10m. Near the sea surface, meteorological and sea condition is significant influence on the gas concentration rather than the other factors.

4.4 Relationship between N_2O and wind speed, wave height

The wave breaking has important role to well mix water near the sea surface. Roughly, the influence of wave breaking reaches deeper than several times the wave height (Drennan 1992). The frequency of wave breaking mainly depends on sea surface wind speed but is partially depends on swell effects. On the equator in the Pacific Ocean, strong swell can be observed from the east end of the Pacific Ocean due to a trade wind and the Antarctic Ocean. So that, the swell effects has important role for gas exchange at air-sea interface.

Relation of the saturation values (SN_2O) for the average velocity of the wind and the significant wave height are shown in **Fig.6**. The spatial averaged N_2O saturation degree is used the mean of 0-50m in depth, and the representative value of the surface area was used and the average velocity of the wind and the significant wave for nine hours averaged value before the water sampling. The large scatter can be observed between the velocity of the wind and SN_2O. Moreover, the relationship between the significant wave height and SN_2O shows similar tendency between the wind speed and SN_2O. This is because that the wave height strongly depends on sea surface wind speed for high wind speed region. However, the correlation coefficient between significant wave height and SN_2O is significantly higher than that value between the wind speed and SN_2O. The main reason is probably effects of swell. The low wind speed condition, the wave enhances gas transfer than wind induced surface renewal. A lot of white caps at wave crests could be observed visually in the condition of low wind speed during the observations. Monahan and Woolf (1989) show that the gas exchange is

promoted with white capping of wind waves and it is thought that there is a possibility of the N_2O re-released from the ocean to atmosphere in equatorial waters. Unfortunately, discussion in detail is impossible, because the observation on waves was conducted only at the significant wave. A detail sea surface measurement is necessary to understand the gas distributions and variations in low wind speed near the sea surface in the future.

5.   Conculusions

The concentration of N_2O on the equator in the Pacific Ocean from sea surface to deep water at January 1999 and December 1999 was observed. Observed concentration of N_2O in the sea surface was about less than 10nM and the maximum value was 40-50nM in depth of 100-500m. Gas concentration variation was not only dependent on the water temperature, but also depends on the sea states, such as wind speed and wave height. The relationship between the significant wave height and SN_2O shows similar tendency between the wind speed and SN_2O. The correlation coefficient between significant wave height and SN_2O is significantly higher than that value between the wind speed and SN_2O.

Acknowledgment

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