High-resolution distribution pattern of surface water nitrous oxide along a cruise track from the Okhotsk Sea to the western Arctic Ocean

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Abstract

Nitrous oxide in the surface water was measured using an automatic underway system, along with measurements of surface water pCO2, dissolved oxygen, salinity, temperature, and sea ice coverage, along a cruise track through the Bering Sea and Chukchi Sea to the Canadian Basin during the 7th Chinese National Arctic Research Expedition. The results show that, overall, the regions along the cruise track are net sources of N2O to the atmosphere. Several N2O oversaturation maxima were observed along the cruise track, with an absolute maximum of approximately 60%. According to the hydrographic setting and the distribution patterns of pCO2, dissolved oxygen, and sea ice coverage in the study area, it was concluded that the N2O oversaturation maxima may result from hydrographic processes, such as mixing of different water masses, upwelling or convection, and possible production beneath the sea ice. Additionally, the lowest value of approximately 90% may result from dilution related to the melting of sea ice. An evaluation of the air–sea flux along the cruise track shows that the continental shelf and upwelling region are N2O sources, whereas the study area in the open Arctic Ocean does not show obvious source or sink characteristics.

Nitrous oxide is one of the more important greenhouse gases and has a greenhouse effect approximately 300 times greater than that of CO2 on a per molecular basis; in addition, N2O is currently the ozone-depleting substance with the largest emission rate (Ravishankara et al. 2009). The ocean is among the most important N2O sources to the atmosphere and accounts for ~21% of the global N2O (Bange et al. 2019). Since the first study on oceanic N2O carried out by Craig and Gordon (1963), this subject has been extensively studied (Bange et al. 2019), and the results show that open oceans are slightly supersaturated with N2O at 104–130% (Dore et al. 1998; Wilson et al. 2014). In the N2O hotspots in the eastern tropical South Pacific Ocean, eastern tropical North Pacific (ETNP) and the Arabian Sea, N2O supersaturation has been identified in the surface water and has been rigorously studied. Arévalo-Martínez et al. (2015) observed a maximum N2O supersaturation of 12,244% in the eastern tropical South Pacific (ETSP), which contributes 5–20% of the global budget. Kock et al. (2015) identified an accumulation of N2O (~850 nM) in the oxygen minimum zone, and Bourbonnais et al. (2017) observed a maximum N2O concentration of ~190 nM in the surface water of the oxygen deficient zone of the same region. Furthermore, Babbin et al. (2015) revealed that the N2O turnover is approximately 20 times higher than that of atmospheric efflux in the ETNP. However, although N2O production is less active in the open ocean than in the hotspots, the open ocean contributes significantly to the global budget (Dore et al. 1998). Details on the N2O source and sink characteristics of hotspot regions, such as the Peruvian upwelling regions (Arévalo-Martínez et al. 2015), and the open ocean, such as the Southern Ocean (Grefe et al. 2018), were further revealed with the development of high-resolution underway observation systems based on off-axis integrated cavity output spectroscopy (Arévalo-Martínez et al. 2013; Grefe and Kaiser 2014) and cavity ring down spectroscopy (Zhan et al. 2018).

The difference in N2O production rates between the open ocean and hotspot regions is due to the different mechanisms present at these locations. In oxic open ocean water,
Nitification is considered the dominant N$_2$O production mechanism (Cohen and Gordon 1979; Bange and Andreae 1999). In the hotspot regions, N$_2$O production is more intense than that in the open ocean because of the low oxygen conditions (oxygen minimum zone, OMZ) resulting from the remineralization of organic particulate matter associated with the high productivity in this region. Nitification may be enhanced at low dissolved oxygen (DO) concentrations (Goreau et al. 1980); however, this phenomenon was not observed in more recent studies using isotope techniques (Frame and Casciotti 2010). Instead, denitification was reported as a major contributor to N$_2$O production under low oxygen conditions (Rabin et al. 2015; Bourbonnais et al. 2017), whereas Ji et al. (2015) revealed coupling of nitification and denitification in the ETSP OMZ region. In addition to canonical denitification that utilizes NO$_3^-$, nitrifier denitification is another denitification process but only reduces NO$_2^-$ to N$_2$O. It may occur not only under low oxygen concentrations but also in the oxygenated lower euphotic zone and upper aphotic zone (Ostrom et al. 2000; Wilson et al. 2014).

Among the studied areas, little is known about the N$_2$O source and sink characteristics of the Arctic Ocean, and only limited studies have been carried out in this area (Hiroti et al. 2009; Kitidis et al. 2010; Fenwick et al. 2017). These studies suggested that N$_2$O oversaturation over the continental shelf may result from nitification, denitification or their coupled processes, whereas N$_2$O undersaturation in surface water can be caused by ice melting (Randall et al. 2012). This work presents the application of an automated high-resolution underway N$_2$O observation system in the Bering Sea, Chukchi Sea and Canadian Basin for the first time during the 7$^{th}$ Chinese National Arctic Expedition (CHINARE), and the source and sink characteristics of the study area are discussed.

**Method and study area**

**Study area and hydrographic setting**

During the 7$^{th}$ CHINARE, which was conducted between early July and late September 2016, the N$_2$O concentration and pCO$_2$ in the surface water between 49$^\circ$N and 78$^\circ$N along the cruise track were measured. The study area is shown in Fig. 1, and the cruise track is marked by a blue line. The R/V Xuelong left the Okhotsk Sea on the 16$^{th}$ of July, entered the Bering Sea via the Aleutian Arc, and left the Bering Sea via the Bering Strait for the Chukchi Sea on the 24$^{th}$ of July. After station sampling was conducted over the Chukchi Plateau, the collection of the data used in this work was completed on the 2$^{nd}$ of Aug.

The current system in the study area is also shown in Fig. 1. The Alaskan Stream (light blue) flows westward along the southern flank of the Aleutian Islands, exchanging water with the Bering Sea via the main sills along the Aleutian Arc. One branch of the system flows along the eastern coast of the Bering Sea into the Arctic Ocean, whereas part of the system flows across the Bering Sea continental slope as the Bering Slope Current (purple), which is also the north limb of the Bering Sea Gyre. This current separates into two branches, one that flows northward and forms the Anadyr current (red) and the other that flows southward and is known as the Kamchatka Current (gray). The Anadyr Current and the Alaskan Coastal Current flow through the Bering Strait. North of the Bering Strait, the inflow waters separate into three main currents that flow through the Herald Canyon, Central Channel, and along the Alaskan coast, and all three currents turn eastward; part of the eastern branch turns west to form the Chukchi Slope Current at Barrow Canyon (light green) (Corlett and Pickart 2017). North of the Pacific-origin water is the eastward-flowing Atlantic-origin water.

**Method for underway observations**

Nitrous oxide and Carbon dioxide data in the air and surface water were continuously measured with an automated underway system consisting of an upstream device and Picarro 5101i N$_2$O isotope and 2131i CO$_2$ isotope analyzers (Picarro). The setting of the instrument was as described in Zhan et al. (2018). Briefly, the automatic underway system was programmed to select gas samples from the equilibrator headspace, atmosphere, and two tanks of mixed N$_2$O and CO$_2$ reference gas. Reference 1 contained 329.4 $\pm$ 0.4 ppb N$_2$O and 409.2 $\pm$ 0.2 ppm CO$_2$, and reference 2 contained 912.5 $\pm$ 0.9 ppb N$_2$O and 685.1 $\pm$ 0.4 ppm CO$_2$. These reference gases were provided by Beijing Huaxin Space & Sky Technology and were calibrated against NOAA reference gas with the 5101i instrument in the laboratory. Surface water was pumped from the water inlet 4.5 m below the surface and passed through the equilibrator at a rate of approximately 500 mL min$^{-1}$ in the upstream device, whereas the closed loop of the gas line ran in the opposite direction at a rate of $\approx$ 500 mL min$^{-1}$. The gas sample then bubbled into the water sample and then passed through a Peltrix dryer and Nafion tube to remove moisture. The analyzers were connected in parallel. The gas line was separated and joined upstream and downstream of the inlet and outlet of the two analyzers using tee connections. The sample gas flowed through the two analyzers at a flow rate controlled by a mass flow rate controller to meet the analyzers' required flow rates. The gas sample then returned to the equilibrator. The N$_2$O measurement results were compared with those obtained using gas chromatography (GC) in the laboratory on land, and the results showed that the underway system data deviate by less than 3% from the data obtained by GC, suggesting that the two methods are consistent with each other. The precision of this method was better than 0.5%. The CO$_2$ data obtained using this method were compared to those obtained using the GO (General Oceanics) Automated Flowing pCO$_2$ Measuring System on the same cruise. The correlations between the data derived from these two methods resulted in a linear correlation of $y = (1.0496 \pm 0.0007)x + (-11.3887 \pm 0.2220)$, with an $R^2$ of 0.9974.
The surface water temperature (SST) and salinity (SSS) were measured using an SBE21 instrument (Sea-Bird Electronics) deployed at the seawater inlet of the research vessel. The SST and SSS along the cruise track are shown in Figs. 2a and S1.

The surface DO was measured by an Aanderaa 4835 optode (Aanderaa Data Instruments AS), which was calibrated against discrete Winkler titrations.

The method for sea ice observation is described as follows. The sea ice concentration (in percentage, $f$) was observed and documented every half-hour using the protocol of the Arctic Shipborne Sea Ice Standardization Tool established by the Climate-Cryosphere Arctic Sea Ice Working Group to characterize typical Arctic conditions. The sea ice observation was performed from the bridge of the R/V Xuelong for a local area with a diameter of 2 km, which might be reduced to 1 km on foggy days. For more detail, refer to Lei et al. (2017) and Hutchings and Faber (2018).

Air–sea flux calculation

The air–sea N$_2$O flux along the cruise track was calculated using the air–sea equation (Liss and Merlivat 1986; Wanninkhof 1992):

$$ F = k \Delta C $$

where $F$ is the air–sea flux of the gas, $k$ is the gas exchange coefficient, and $\Delta C$ is the difference between the observed concentration in and equilibrium concentration of the surface water calculated from the atmospheric partial pressure and in situ conditions, such as surface water temperature, salinity, and atmospheric pressure. Since the above studies evaluated open water, the above equations were all multiplied by the percentage of open water, which was expressed as $1-f$, where $f$ represents the sea ice concentration.

The gas exchange coefficient of the whole cruise track was evaluated using the equations of Ho et al. (2006) and Nightingale et al. (2000).

$$ k = 0.266 U_{10}^{2} \left( \frac{Sc}{600} \right)^{-\frac{1}{2}} \quad (2) $$

$$ k = (0.222 U_{10}^{2} + 0.333 U_{10}) \left( \frac{Sc}{600} \right)^{-\frac{1}{2}} \quad (3) $$

According to van der Loeff et al. (2014), the presence of sea ice blocks air–sea exchange, and the Arctic Ocean is partially covered by sea ice. Thus, the gas exchange coefficient of open water in this region was also evaluated with the equation proposed by van der Loeff et al. (2014):

$$ k = 0.074 U_{10}^{2} \left( \frac{Sc}{600} \right)^{-\frac{1}{2}} \quad (4) $$

$U_{10}$ is the wind speed above sea level and Sc is the Schmidt number, which is defined as the kinematic viscosity of the
water divided by the diffusion coefficient of the gas and can be calculated following Wanninkhof (2014).

For the wind speed data, we used the remote sensing wind speed product from ASCAT (https://podaac-tools.jpl.nasa.gov) with a spatial resolution of 25 km. Taking into account the nonlinearity of the wind speed parameterization, the weighted gas exchange coefficient was calculated from the 60 daily wind speed data prior to the measuring time using the function developed by Reuer et al. (2007). The weighting is based on the fraction of the mixing layer ventilated on any given date (Fenwick et al. 2017). The mixed layer depth product was utilized, which could be obtained from global ocean physics reanalysis from CMEMS (Copernicus marine environment management service, http://marine.copernicus.edu/) with a high spatial resolution of 1/12° according to the collection dates.

**Results and discussion**

**Distribution of N2O along the cruise track**

The distribution of N2O along the cruise track is shown in Fig. 2b. Except for several maxima along the whole cruise track, the N2O concentration shows a trend of increasing from 11.0 to ~ 16.5 nM, which results from the increasing solubility of a gas with the decline in SST. When the N2O concentration was plotted against the SST (Fig. 3), most of the N2O concentration data are above the equilibrium line (red solid line), indicating that nearly all the surface water of the whole cruise track is oversaturated with N2O; in particular, at the high- and low-temperature ends, the surface water shows a state of N2O oversaturation.

To further reveal the source and sink characteristics of the study area, the saturation anomaly (SA) was calculated using the following equation:
The cruise track was located in the open Arctic Ocean (north of 4700 km), where the N2O in the surface water is significantly influenced by the ice melting process. The mechanisms of N2O SA maximum formation are discussed according to these categories in the following sections.

Open sub-Arctic basin (leg 1)

Three maxima were observed on leg 1. The first maximum (maximum 1) was observed at 339 km between the Okhotsk Sea and the Pacific. The N2O concentration in the surface water of this maximum was 15.7 nM, which was ~2 nM higher than that of the adjacent seas, and the N2O SA value was 20%. The water depth at this N2O SA maximum was more than 1000 m, and the SSS maximum present at this location suggested that this N2O oversaturation should not be contributed by continental shelf emission or terrigenous riverine discharge. It was reported that the Kamchatka Current flows southward into the Okhotsk Sea via paths between the Kuril Islands in this region (Tomczak and Godfrey 1994). This inflow current turns northeast after entering the Okhotsk Sea, which results in the southwestward transport of surface water due to the Coriolis effect and subsequent upwelling, which may bring N2O-enriched deep water to the surface and result in the N2O SA maximum 1. Deeper water enriched in N2O is generally also enriched with CO2, depleted in oxygen, and characterized by a relatively low temperature and high salinity. These signals were all observed at this location (Fig. 2a,e,f), indicating that upwelling may be a source that contributes to the N2O SA maximum 1.

Maximum 2 was a relatively weak maximum of approximately 13% (Fig. 2c). The distribution of pCO2 over the same

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SA = \frac{C_{ob} - C_{eq}}{C_{ob}} \times 100
\]

where \(C_{ob}\) is the observed N2O concentration and \(C_{eq}\) is the equilibrium concentration calculated from the in situ SST, SSS, atmospheric pressure, and atmospheric N2O mixing ratios. The derived SA of the whole cruise track was plotted against section distance (Fig. 2c). Except for the maxima along the cruise track, the rest of the surface water SA value was regarded as the SA baseline and can be divided into two parts: south of 4700 km, where the SA baseline ranged between 4% and 10%, which is consistent with other studies (Wilson et al. (2014) and references therein), and north of 4700 km, where the SA baseline is approximately 0%. The difference south and north of 4700 km probably results from different surface water properties. South of 4700 km, the surface water was influenced by different hydrographic structures, such as fronts, upwelling, and possible sediment release of N2O, which can reach or even outcrop the surface water, whereas north of 4700 km, the surface water is homogeneous in properties and well stratified due to the ice melting process, resulting in N2O near equilibrium in the surface water. This cruise was conducted in summer when the surface water was warming up. The SST of the cruise track on the 24th of June and 24th of July 2016 were selected by interpolating the SST data from AVHRR (Advanced Very High Resolution Radiometer, http://apdrc.soest.hawaii.edu). The 24th of July was chosen because it is the middle date of this cruise track. The maximum SST difference (\(\Delta T\)) is ~4°C between these 2 months (Fig. 2d). Although the \(\Delta T\) is a snapshot of the temperature change between June and July, it indicates that in the open water along the cruise track, the 4°C warming of the surface water at this latitude will lead to a maximum 15% decline in the N2O solubility according to the study on N2O solubility carried out by Weiss and Price (1980). However, the air–sea exchange was ongoing during this month, which replenished the surface water with atmospheric N2O. This exchange process is slower than that of air–sea heat exchange and therefore leads to seasonal N2O saturation anomalies (Butler et al. 1989). However, previous studies have shown that the oversaturation resulting from this seasonal effect should be less than 4% (Nevison et al. 1995). Therefore, for the open water on the cruise track, if a maximum seasonal effect of 4% was taken into account, the baseline of the SA is 0–6%, which indicates that the study region is a weak N2O source as a whole.

To further discuss the distribution pattern and the corresponding mechanisms, the cruise track was divided into three legs according to the characteristics of the study regions it passed through. Leg 1: The cruise track was located in the open subpolar ocean (between the starting point and 3000 km) and passed through part of the Okhotsk Sea, the Northwest Pacific, and the Aleutian Basin. The N2O in the surface water in these regions is generally regulated by hydrographic processes. Leg 2: The cruise track was located on the continental shelf (between 3000 and 4700 km), where possible sediment emissions may contribute N2O to the surface water (Hirota et al. 2009), and it passed through the Bering Sea continental shelf, Bering Strait, and Chukchi Sea. Leg 3: The cruise track was located in the open Arctic Ocean (north of 4700 km), where the N2O in the surface sea water is significantly influenced by the ice melting process. The mechanisms of N2O SA maximum formation are discussed according to these categories in the following sections.
spatial range showed a remarkable increase in pCO2 from 226 to 407 ppm north of 1000 km, and the oxygen saturation and SST values also showed turning points. Sharp changes in physical and chemical signals generally mark the presence of divergence, convergence or fronts. Therefore, a front may exist at this location. Butler et al. (1989), Grege et al. (2018), and Rees et al. (1997) also show that N2O saturation may be elevated or variable at fronts. Elevated saturation levels may result from the water mixing process at the frontal structure (Rees et al. 1997), where a sharp change in temperature leads to a sharp change in gas solubility, or due to the presence of eddies (Rees et al. 1997), which uplift N2O-rich deeper water and lead to surface water N2O oversaturation. However, this variation or elevation of N2O saturation is not identified at all fronts that have been observed (Rees et al. 1997). With only limited high-resolution data available, the dynamics of N2O at fronts need to be further addressed.

The 3rd maximum along leg 1 was located at the northwestern end of the cruise track and was among the most significant N2O SA maxima of the whole cruise track. The observed N2O SA at this maximum was ~ 60%. This N2O SA maximum corresponded to a salinity and temperature minimum, which were approximately 1°C and 1.4 lower than the SST and SSS values of the adjacent region, respectively (Fig. 2a). Moreover, the corresponding pCO2 at this location was the lowest of Leg 1, with a minimum of approximately 170 ppm. However, the DO did not show a remarkable supersaturation maximum. Decreasing SST and SSS values indicated that the cruise track may have coincided with the Kamchatka Current (Rogachev 2000), which may be enriched in N2O. When it flows southward, it becomes warmer and shows oversaturation of N2O. Another possibility is upwelling of subsurface water, which resulted from the passage of a cyclone over this location. The cyclone may have uplifted colder and N2O-enriched water to the surface layer, leading to surface water N2O oversaturation. However, subsurface water generally contains high concentrations of CO2, which may also lead to CO2 oversaturation. One possible explanation for the pCO2 minimum observed at this location may be the rapid consumption of CO2 by photosynthesis.

Continental Shelf (leg 2)
Over the continental shelf, four N2O SA maxima (4, 5, 6, and 7) ranging between 15% and 37% can be identified along leg 2. Since this leg is on the continental shelf, these maxima may be related to continental sediment emissions. Hirota et al. (2009) observed increasing concentrations of N2O with depth in the Bering Sea and concluded that the N2O over the Bering Sea continental shelf may be related to denitrification. The DO concentration in the water column is not low enough to initiate denitrification; thus, the sediment may provide a location for denitrification, which was previously observed in the Bering Sea sediment (Horak et al. 2013). Our results show that the SA maxima can be divided into two categories according to the corresponding pCO2 and DO distribution patterns. The pCO2 and DO distribution patterns are opposite in maxima between these two groups, with maximum 5 presenting a pCO2 maximum and DO minimum and maxima 4, 6, and 7 presenting a pCO2 minimum and DO maximum.

At nitrous oxide SA maximum 5 (SA ~ 28%), the SST suddenly dropped from 11.3°C to 1.7°C, which was also shown by the NOAA AVHRR data (http://apdrc.soest.hawaii.edu/data/data.php). A large area of low SSTs was observed north of St. Lawrence Island, and the SSS increased from 30.1 to 32.6; thus, this region presented the lowest temperature and highest salinity on the ice-free continental shelf. The corresponding pCO2 maximum, ~ 537 ppm, was the absolute maximum and the only source of CO2 to the atmosphere along this cruise track. In addition, the only instance of DO undersaturation (~ 88%) was also observed at this location (Fig. 2f). This cold water region was reported by Nihou (1986), who observed a front and upwelling west of the front. This upwelling can bring nutrient-rich bottom water to the surface in the western region north of St. Lawrence Island. Hence, it can be concluded that the upwelling at this site brought the bottom water, which was cold, contained high concentrations of N2O and CO2 but was depleted of DO, to the near surface, resulting in the surface water N2O SA maximum.

The nitrous oxide SA maximum 6 (SA ~ 21%) also corresponds to the SST minimum of ~ 4.7°C and a salinity of ~ 32.4. The variable SST and SSS around this maximum indicate that the cruise track probably crossed different water masses in the Chukchi Sea. According to Bates et al. (2006), the relatively fresh, warm, nutrient-depleted Alaskan Coastal Current is located in the east, and the relatively cold, salty, and nutrient-rich Anadyr Water (AW) is located in the west. Therefore, between these two water masses is a front, where the mixing process may enhance convection, bring N2O bottom water into the surface layer and result in this maximum. Furthermore, this bottom water is also nutrient-rich, promoting productivity at the front. Therefore, CO2 is quickly consumed, and DO is produced, resulting in the pCO2 minimum and DO maximum and resulting in pCO2 and DO distribution patterns opposite those observed at maximum 5.

The nitrous oxide SA maximum 7, with an SA value of ~ 37%, has a similar pCO2 minimum and DO saturation pattern as maximum 6; however, the pCO2 minimum and DO saturation maximum were the absolute minimum and maximum values of the whole cruise track, indicating the enhanced primary production present at this location. Moreover, the SST at this location experienced a remarkable decrease to approximately ~0.4°C, which was close to the lowest SST value on the cruise track, and the SSS was as low as 21.0, which was also the lowest salinity of the whole cruise track. The N2O O maximum of approximately 23 nM, together with the SA, indicated that this oversaturation does not result from the temperature effect. Regarding the sea ice distribution...
pattern (Fig. 2d), a high density of sea ice was observed for the first time on the cruise track at this site, indicating that this site was in the melting sea ice zone (MIZ).

Multiple processes and mechanisms may contribute to N2O oversaturation. Hydrographic processes are one of the processes leading to oversaturation. The existence of the eastward-flowing currents in the Chukchi Sea and the westward-flowing Chukchi Slope Current (Fig. 1) together may result in divergence at this location and bring subsurface water with high N2O concentrations (Zhang et al. 2015; Wu et al. 2017) to the surface layer, resulting in N2O oversaturation. However, the observed SST and SSS minima also indicate an ongoing ice melting process, which may dilute the surface water N2O concentration and even lead to N2O undersaturation. Wu et al. (2017) and Zhang et al. (2015) both observed N2O undersaturation at this location. This discrepancy between these studies may result from different observation times. Both Wu et al. (2017) and Zhang et al. (2015) carried out studies in late summer. When ice melting prevails, surface water is diluted by meltwater, and stratification develops, which nearly inhibits the exchange between subsurface and surface water. Hence, eddy diffusion can contribute only a very limited amount of N2O from subsurface water to surface water, and the surface water remains undersaturated or near equilibrium in terms of N2O. However, during early summer, when our underway observation was carried out, the ice melting process may not be significant enough to dilute the surface water, and the surface water is still in a state of N2O oversaturation.

Another possible process contributing to this oversaturation may be in situ production near the surface water or sea ice. A similar phenomenon of N2O oversaturation in the MIZ was also observed in Baffin Bay by Kitidis et al. (2010), who suggested it was the result of organic matter mineralization. Moreover, they also observed high N2O concentrations under multiyear ice, and this N2O may be emitted to the atmosphere when the sea ice retreats. Studies have suggested that production beneath sea ice may occur. Rysgaard and Glud (2004) suggested that denitrification in sea ice can also be a possible source for N2O; Baer et al. (2014) found nitriﬁcation to be stronger in winter than in summer, which may also result in N2O trapped beneath the sea ice.

In summary, the N2O SA maximum on leg 2 may result from uplift of N2O-rich bottom water over the continental shelf to the surface layer by upwelling or convection accompanying the frontal mixing process. Furthermore, the denitrification and nitrification processes in ice-covered areas may also be possible mechanisms that need to be explored.

Open Arctic Ocean (leg 3)

The nitrous oxide SA along leg 3 was close to zero, indicating that the N2O in the surface water throughout most of this leg was near equilibrium with the atmosphere. With the presence of sea ice, the SST remained relatively stable and ranged between −1.0°C and 1.2°C, whereas the salinity ranged between 23.60 and 27.60 (Fig. 2d). Except for N2O maximum 8, the N2O SA value along this leg centered on zero showed no obvious source or sink characteristics overall. The corresponding pCO2 of this leg was approximately 370 ppm, and the DO in the surface water was in equilibrium with the atmosphere, suggesting that the primary production along

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**Table 1.** The air–sea fluxes of different legs of the study area.

| Leg   | $F_H$ (± SD) | $F_N$ (± SD) | $F_L$ (± SD) |
|-------|--------------|--------------|--------------|
| Leg 1 | 2.3±2.2      | 2.3±2.2      | —            |
| Leg 2 | 3.7±5.0      | 3.7±5.1      | —            |
| Leg 3 | 0.24±0.31    | 0.24±0.31    | 0.08±0.10    |

$F_H$, $F_N$, and $F_L$ are the fluxes calculated using Ho et al. (2006), Nightingale et al. (2000), and van der Loeff et al. (2014), respectively.
this leg was also low. The low primary production and net community production were described by Tremblay et al. (2015), and these conditions may not support significant N$_2$O production in the subsurface water. The N$_2$O SA maximum of approximately 34% corresponds to a pCO$_2$ minimum of approximately 313 ppm, which may also be MIZ-related N$_2$O oversaturation. N$_2$O undersaturation occurred with an SA value of approximately −9% at 4800 km, which corresponds to one of the temperature minima (−1.0°C) and a low salinity of approximately 25.02. Studies have shown that the N$_2$O concentration in Arctic sea ice is only ~ 6 nM (Randall et al. 2012); therefore, when the ice melts, it may dilute the surface water and result in surface water N$_2$O undersaturation before returning to equilibrium again.

Compared with the first two legs, leg 3 shows a different N$_2$O SA distribution pattern, and the study area on this leg is the largest area with a near-equilibrium N$_2$O concentration. The ice melting process is probably the main reason for the N$_2$O saturation state observed in the surface water along this leg.

**Air-sea flux along the cruise track**

According to Fenwick et al. (2017), the air–sea flux evaluated from instantaneous wind speed data leads to a positive bias. Our result calculated from instantaneous wind speed also shows overestimation of the air–sea flux (result not shown). Therefore, to derive a more reasonable seasonal flux, the weighted air–sea exchange coefficient (Reuer et al. 2007) was calculated based on the functions suggested by Ho et al. (2006), Nightingale et al. (2000) and Van Der Loeff et al. (2014). With the weighted air–sea exchange coefficient, the air–sea fluxes derived from these methods are shown in Fig. 4. The gray dot and black dots are the results calculated from Ho et al. (2006) and Nightingale et al. (2000), respectively, which showed no and black dots are the results calculated from Ho et al. (2006) derived from these methods are shown in Fig. 4. The gray dot represents an average sea-to-air flux of $\frac{1.0}{1.0}$, and Nightingale et al. (2000) are similar, and all three parameterizations indicate that the open Arctic Ocean shows no obvious source and sink characteristics during summer.

Compared with the results reported by Hirota et al. (2009) and Fenwick et al. (2017), the air–sea flux values for the Bering Sea and Chukchi Sea reported here are higher than those reported by Fenwick et al. (2017) but similar to those reported by Hirota et al. (2009). A possible explanation for the difference between our result and that of Fenwick et al. (2017) over the continental shelf is that the high concentration of the surface water maximum may not be captured by the station sampling method since the distribution of N$_2$O in the continental shelf sea water is inhomogeneous. However, these maxima are best captured by the high-resolution underway method. The similarity of the open Arctic Ocean N$_2$O air–sea fluxes between Fenwick et al. (2017) and this study may be due to the relatively homogeneous distribution of surface water in this region; thus, the station sampling method can provide representative results.

**Conclusions**

In this study, N$_2$O and CO$_2$ along a cruise track between the Bering Sea and Canadian Basin were observed using an underway method based on a cavity ring down system. The surface water along the cruise is a N$_2$O source as a whole, and the results identified numerous N$_2$O SA maxima and only one obvious region of undersaturation (~ 90% saturation), which may have resulted from dilution by melting ice. Several processes or formation mechanisms contribute to these N$_2$O SA maxima: (1) certain hydrographic structures, such as convergence, divergence or fronts, which lead to elevated N$_2$O SA values; (2) convection over the continental shelf, which brings N$_2$O-rich bottom water to the surface and results in a N$_2$O SA maximum and increased pCO$_2$ and decreased DO values; and (3) possible near-surface water N$_2$O production. The third phenomenon can be observed in the MIZ, although further study is needed to reveal its mechanism. The air–sea flux evaluation results showed that the continental shelf presents the highest sea-to-air N$_2$O flux along the cruise track, which is likely associated with N$_2$O-rich deep water brought to the surface by upwelling and convection. The Bering Sea and Chukchi Sea continental shelf may be an important N$_2$O source to the atmosphere, whereas the open Arctic Ocean did not show source or sink characteristics during the study season due to sea ice melting and the subsequent stratification of the water column.

**References**

Arévalo-Martínez, D. L., A. Kock, C. R. Löscher, R. A. Schmitz, and H. W. Bange. 2015. Massive nitrous oxide emissions from the tropical South Pacific Ocean. Nat. Geosci. 8: 530–533.

Arévalo-Martínez, D. L., M. Beyer, M. Krumbholz, I. Piller, A. Kock, T. Steinhoff, A. Körtzinger, and H. W. Bange. 2013. A new method for continuous measurements of oceanic and atmospheric N$_2$O, CO and CO$_2$: Performance of off-axis integrated cavity output spectroscopy (OA-ICOS) coupled...
to non-dispersive infrared detection (NDIR). Ocean Sci. 9: 1071–1087.
Babin, A. R., D. Bianchi, A. Jayakumar, and B. B. Ward. 2015. Rapid nitrous oxide cycling in the suboxic ocean. Science 348: 1127–1129.
Baer, S. E., T. L. Connelly, R. E. Sipler, P. L. Yager, and D. A. Bronk. 2014. Effect of temperature on rates of ammonium uptake and nitrification in the western coastal Arctic during winter, spring, and summer. Global Biogeochem. Cycles 28: 1455–1466.
Bange, H. W., and others. 2019. A harmonized nitrous oxide (N2O) ocean observation network for the 21st century. Front. Mar. Sci. 6: 157.
Bange, H. W., and M. O. Andreae. 1999. Nitrous oxide in the deep waters of the world’s oceans. Global Biogeochem. Cycles 13: 1127–1135.
Bates, N. R., S. B. Moran, D. A. Hansell, and J. T. Mathis. 2006. An increasing CO2 sink in the Arctic Ocean due to sea-ice loss. Geophys. Res. Lett. 33: L23609.
Bourbonnais, A., R. T. Letscher, H. W. Bange, V. Échevin, J. Larkum, J. Mohn, N. Yoshida, and M. A. Altabet. 2017. N2O production and consumption from stable isotopic and concentration data in the Peruvian coastal upwelling system. Global Biogeochem. Cycles 31: 678–698.
Butler, J. H., J. W. Elkins, T. M. Thompson, and K. B. Egan. 1989. Tropospheric and dissolved N2O of the west Pacific and east Indian Oceans during the El Niño Southern Oscillation event of 1987. J. Geophys. Res. Atmos. 94: 14865–14877.
Cohen, Y., and L. I. Gordon. 1979. Nitrous oxide production in the ocean. J. Geophys. Res. 84: 347, C1.
Corlett, W. B., and R. S. Pickart. 2017. The Chukchi slope current. Prog. Oceanogr. 153: 50–65.
Craig, H., and L. I. Gordon. 1963. Nitrous oxide in the ocean and the marine atmosphere. Geochim. Cosmochim. Acta 27: 949–955.
Dore, J. E., B. N. Popp, D. M. Karl, and F. J. Sansone. 1998. A large source of atmospheric nitrous oxide from subtropical North Pacific surface waters. Nature 396: 63–66.
Fenwick, L., D. Capelle, E. Damm, S. Zimmermann, W. J. Williams, S. Vagle, and P. D. Tortell. 2017. Methane and nitrous oxide distributions across the North American Arctic Ocean during summer, 2015. J. Geophys. Res. Oceans 122: 390–412.
Frame, C. H., and K. L. Casciotti. 2010. Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium. Biogeoosciences 7: 2695–2709.
Goreau, T. J., W. A. Kaplan, S. C. Wofsy, M. B. McElroy, F. W. Valois, and S. W. Watson. 1980. Production of NO2 and N2O by nitrifying bacteria at reduced concentrations of oxygen. Appl. Environ. Microbiol. 40: 526–532.
Greene, I., and J. Kaiser. 2014. Equilibrator-based measurements of dissolved nitrous oxide in the surface ocean using an integrated cavity output laser absorption spectrometer. Ocean Sci. 10: 501–512.
Grefe, I., S. Fielding, K. J. Heywood, and J. Kaiser. 2018. Nitrous oxide variability at sub-kilometre resolution in the Atlantic sector of the Southern Ocean. Peerj 6: e5100.
Hirota, A., A. Ijiri, D. K. Komatsu, S. B. Ohkubo, F. Nakagawa, and U. Tsunogai. 2009. Enrichment of nitrous oxide in the water columns in the area of the Bering and Chukchi Seas. Mar. Chem. 116: 47–53.
Ho, D. T., C. S. Law, M. J. Smith, P. Schlosser, M. Harvey, and P. Hill. 2006. Correction to “Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations”. Geophys. Res. Lett. 33: L16611.
Horak, R. E. A., H. Whitney, D. H. Shull, C. W. Mordy, and A. H. Devol. 2013. The role of sediments on the Bering Sea shelf N cycle: Insights from measurements of benthic denitrification and benthic DIN fluxes. Deep-Sea Res. II Top. Stud. Oceanogr. 94: 95–105.
Hutchings, J. K., and M. K. Faber. 2018. Sea-ice morphology change in the Canada basin summer: 2006–2015 ship observations compared to observations from the 1960s to the early 1990s. Front. Earth Sci. 6: 123.
Ji, Q., A. R. Babin, A. Jayakumar, S. Oleynik, and B. B. Ward. 2015. Nitrous oxide production by nitrification and denitrification in the Eastern Tropical South Pacific oxygen minimum zone. Geophys. Res. Lett. 42: 10,755–10,764.
Kitidis, V., R. C. Upstill-Goddard, and L. G. Anderson. 2010. Methane and nitrous oxide in surface water along the North-West Passage, Arctic Ocean. Mar. Chem. 121: 80–86.
Kock, A., D. L. Arévalo-Martínez, C. R. Löschner, and H. W. Bange. 2015. Extreme N2O accumulation in the coastal oxygen minimum zone off Peru. Biogeosciences 13: 827–840.
Lei, R., X. Tian-Kunze, B. Li, P. Heil, J. Wang, J. Zeng, and Z. Tian. 2017. Characterization of summer Arctic sea ice morphology in the 135°–175°W sector using multi-scale methods. Cold Reg. Sci. Technol. 133: 108–120.
Liss, P. S., and L. Merlivat. 1986. Air-sea gas exchange rates: Introduction and synthesis, p. 113–127. In P. Buat-Ménard [ed.], The role of air-sea exchange in geochemical cycling. Springer.
Nevison, C. D., R. F. Weiss, and D. J. Erickson. 1995. Global oceanic emissions of nitrous oxide. J. Geophys. Res. 100: 15809–15820.
Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard. 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. Global Biogeochem. Cycles 14: 373–387.
Nihoul, J. C. J. 1986. Aspects of the Northern Bering Sea ecohydrodynamics, p. 385–399. In J. C. J. Nihoul [ed.], Marine interfaces ecohydrodynamics. Elsevier.
Ostrom, N. E., M. E. Russ, B. Popp, T. M. Rust, and D. M. Karl. 2000. Mechanisms of nitrous oxide production in the subtropical North Pacific based on determinations of the isotopic abundances of nitrous oxide and di-oxygen. Chemosphere Global Change Sci. 2: 281–290.

Randall, K., M. Scarratt, M. Levasseur, S. Michaud, H. Xie, and M. Gosselin. 2012. First measurements of nitrous oxide in Arctic sea ice. J. Geophys. Res.: Oceans 117: C00G15.

Ravishankara, A. R., J. S. Daniel, and R. W. Portmann. 2009. Nitrous oxide (N2O): The dominant ozone-depleting substance emitted in the 21st century. Science 326: 123–125.

Rees, A. P., N. J. P. Owens, and R. C. Upstill-Goddard. 1997. Nitrous oxide in the Bellingshausen Sea and Drake Passage. J. Geophys. Res.: Oceans 102: 3383–3391.

Reuer, M. K., B. A. Barnett, M. L. Bender, P. G. Falkowski, and M. B. Hendricks. 2007. New estimates of Southern Ocean biological production rates from O2/Ar ratios and the triple isotope composition of O2. Deep-Sea Res. I Oceanogr. Res. Pap. 54: 951–974.

Rogachev, K. A. 2000. Recent variability in the Pacific western subarctic boundary currents and Sea of Okhotsk. Prog. Oceanogr. 47: 299–336.

Rysgaard, S., and R. N. Glud. 2004. Anaerobic N2 production in Arctic sea ice. Limnol. Oceanogr. 49: 86–94.

Tomczak, M., and J. S. Godfrey. 1994. Regional oceanography. Elsevier.

Tremblay, J.-É., L. G. Anderson, P. Matrai, P. Coupel, S. Bélanger, C. Michel, and M. Reigstad. 2015. Global and regional drivers of nutrient supply, primary production and CO2 drawdown in the Changing Arctic Ocean. Prog. Oceanogr. 139: 171–196.

van der Loeff, M. M. R., N. Cassar, M. Nicolaus, B. Rabe, and I. Stimac. 2014. The influence of sea ice cover on air-sea gas exchange estimated with radon-222 profiles. J. Geophys. Res.: Oceans 119: 2735–2751.

Wanninkhof, R. 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. 97: 7373–7382, C5.

Wanninkhof, R. 2014. Relationship between wind speed and gas exchange over the ocean revisited. Limnol. Oceanogr.: Methods 12: 351–362.

Weiss, R. F., and B. A. Price. 1980. Nitrous oxide solubility in water and seawater. Mar. Chem. 8: 347–359.

Wilson, S. T., D. A. del Valle, M. Segura-Noguera, and D. M. Karl. 2014. A role for nitrite in the production of nitrous oxide in the lower euphotic zone of the oligotrophic North Pacific Ocean. Deep-Sea Res. I Oceanogr. Res. Pap. 85: 47–55.

Wu, M., L. Chen, L. Zhan, J. Zhang, Y. Li, and J. Liu. 2017. Spatial variability and factors influencing the air-sea N2O flux in the Bering Sea, Chukchi Sea and Chukchi Abyssal Plain. Atmos. 8: 65.

Zhan, L., J. Zhang, Y. Li, M. Wu, J. Liu, Q. Lin, and C. Liqi. 2018. A fully automatic system for underway N2O measurements based on cavity ring-down spectroscopy. Int. J. Environ. Anal. Chem. 98: 709–724.

Zhang, J., L. Zhan, L. Chen, Y. Li, and J. Chen. 2015. Coexistence of nitrous oxide undersaturation and oversaturation in the surface and subsurface of the western Arctic Ocean. J. Geophys. Res.: Oceans 120: 8392–8401.

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Conflict of Interest

None declared.

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