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Key Points:
• Temporal variations in isotopic ratios of atmospheric N₂O from Taiwan
• Isotopic ratio increase is concurrent with strengthening of the subtropical jet
• Positive trends suggest intrusion of air from the stratosphere

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Abstract We present analyses of nitrogen and oxygen isotopic ratios and site-preference (SP) values of atmospheric nitrous oxide samples obtained from Taiwan in west Pacific. Air samples were collected during September 2013 to January 2016 from Taipei and during November 2011 to December 2014 from Keelung, located in the northeastern coast of Taiwan. The average values of δ¹⁵N, δ¹⁸O, and SP are 6.4 ± 0.3 ‰, 44.0 ± 0.4 ‰, and 17.1 ± 1.0 ‰, respectively, at Taipei and 6.4 ± 0.2 ‰, 44.6 ± 0.4 ‰, and 17.9 ± 1.3 ‰, for δ¹⁵N, δ¹⁸O, and SP respectively, at Keelung, comparable to the average values (6.6 ± 0.2, 44.2 ± 0.2, and 18.1 ± 0.5 ‰, scaled to year 2014) from Hateruma, an open ocean station in western Pacific. Strong temporal variations in the delta values, however, are seen. During a subtropical jet-strengthening period in October to mid-December 2014, the δ¹⁵N, δ¹⁸O and SP values increased at the rate of 0.006 ± 0.002 ‰/day, 0.010 ± 0.002 ‰/day and 0.008 ± 0.002 ‰/day, respectively at Taipei and 0.013 ± 0.005 ‰/day, 0.011 ± 0.005 ‰/day and 0.011 ± 0.027 ‰/day at Keelung. This suggests intrusion of air to the lower troposphere from the stratosphere where δ¹⁵N, δ¹⁸O and SP values are higher. This is consistent with earlier observations of oxygen isotope anomaly in atmospheric CO₂ and elevated ³⁵S in sulfate aerosols, indicating frequent stratospheric intrusions in this region. The observed δ¹⁵N and δ¹⁸O values, along with the oxygen isotope anomaly in CO₂ and multiple sulfur isotopes in sulfate, can be used to constrain local emissions from the surface, improving our knowledge of anthropogenic contribution to the global budget of N₂O.

1. Introduction

N₂O is one of the important trace gases present in the Earth’s atmosphere. It is a major greenhouse gas with global warming potential ~300 times higher than that of CO₂ (Thornes, 2002) on a per molecule basis. In addition, it has a major role in stratospheric chemistry since N₂O is the main source of stratospheric NO, which catalytically destroys ozone (Crutzen & Quart, 1970). During the preindustrial era, tropospheric N₂O concentration was ~270 nmol/mol, which has increased to 327 ± 0.1 nmol/mol in 2014 (WMO (World Meteorological Organization), 2015). During the last 10 years, the annual rate of increase of atmospheric N₂O is 0.87 nmol/mol per year on average (WMO (World Meteorological Organization), 2015). This is mainly due to increase in anthropogenic activities like agriculture and fossil fuel combustion (Khalil et al., 2002; Machida et al., 1995; Park et al., 2012). Therefore, it is deemed essential to estimate the global N₂O budget with accuracy. This will help in planning the mitigation strategies to stem the rise of N₂O in the atmosphere.

The sources of N₂O are both natural and anthropogenic which include soils (via nitrification and denitrification processes), automobile exhaust, fresh water or ocean, livestock, industrial processes, fossil fuel combustion, biomass burning, etc. (e.g., see Prather & Ehhalt, 2001). The major sink of N₂O is in the stratosphere where it is chemically destroyed by photolysis (90%) and reaction with electronically excited oxygen atoms (10%) (Cliff & Thiemens, 1997; Kim & Craig, 1993; Minschwaner et al., 1993; Rahn & Wahlen, 1997). However, significant uncertainty remains in the quantification of the N₂O fluxes from/to the different reservoirs (e.g., see Toyoda et al., 2013).

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The bulk nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) isotope ratios of $\text{N}_2\text{O}$ have been shown to be different for different precursor materials and the signatures of physiochemical processes they undergo are often used to infer the global $\text{N}_2\text{O}$ budget using an isotope mass balance approach (Kim & Craig, 1993; Rahn & Wahlen, 2000; Toyoda et al., 2013; Yoshida & Matsuo, 1983). Additionally, high precision measurements of intramolecular distribution of $^{15}\text{N}$ in the asymmetric $\text{N}_2\text{O}$ molecule, termed as site preference, SP, also serve as a powerful tool to identify the $\text{N}_2\text{O}$ flux from individual reservoirs with characteristic SP values, in particular the partitioning between nitrification and denitrification. The SP values of individual reservoirs like the atmosphere (Kaiser et al., 2003; Toyoda et al., 2001, 2004; Yoshida & Toyoda, 2000), ocean (Toyoda et al., 2002) and stratosphere (Kaiser et al., 2006; McLinden et al., 2003; Morgan et al., 2004; Toyoda et al., 2013 and references therein) and sources like soil emissions (Pérez et al., 2001; Suitka et al., 2003; Yamulki et al., 2001) and automobile exhausts (Toyoda et al., 2008) have been constrained by earlier studies. Beside the source isotope differences, various sink processes are also associated with different isotopic fractionations (Kim & Craig, 1993; Yung & Miller, 1997). At the present state of knowledge, there is an imbalance between the sources and sinks of $\text{N}_2\text{O}$, to the extent of about $4.0 \pm 0.5 \text{TgN/yr}$ (Intergovernmental Panel on Climate Change (IPCC), 2007), reffecting the trend in the atmosphere. In this context, combined measurements of bulk isotopic ratios ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and site preference (SP) values of $\text{N}_2\text{O}$ can be utilized to refine the global budget of $\text{N}_2\text{O}$ with high accuracy (Park et al., 2012; Rahn & Wahlen, 2000; Toyoda et al., 2013; Yoshida & Toyoda, 2000).

Among the important greenhouse gases ($\text{N}_2\text{O}$, $\text{CO}_2$ and $\text{CH}_4$), our understanding of the isotopic budget of $\text{N}_2\text{O}$ lags far behind the others. Due to its long atmospheric lifetime of ~120 years (IPCC, 2001), it is generally believed that $\text{N}_2\text{O}$ distribution is rather uniform over the globe (within 2 nmol/mol; e.g., see Prinn et al., 2000, Jiang et al., 2007). Therefore, seasonal and spatial variations that may give insight into the isotopic budget are less perceptible in case of $\text{N}_2\text{O}$ (e.g., see Kaiser et al., 2003) unlike other trace gases like $\text{CO}_2$ (Graven et al., 2013). Attempts have been made to improve the precision of the measurements to detect minor variations, and indeed recent advances can help to gain insight into the budget and $\text{N}_2\text{O}$ flux estimation from various reservoirs (Toyoda et al., 2013). While addressing the global fluxes of $\text{N}_2\text{O}$, it is essential to have scale consistency in analysis among different laboratories, i.e., the data generated from different laboratories worldwide should be reported with respect to a common reference scale. However, unlike $\text{CO}_2$ there is no international standard for $\text{N}_2\text{O}$. Recently, a cooperative initiative was taken to circulate several $\text{N}_2\text{O}$ samples with known isotopic ratios between laboratories worldwide (Mohn et al., 2014). This exercise allowed identification of analytical offset of an individual laboratory from others and bring all the laboratories into the same scale.

The isotopic ratios of tropospheric $\text{N}_2\text{O}$ have been reported by many investigators since the mid-1970s (Kaiser et al., 2003; Kim & Craig, 1990, 1993; Moore, 1974; Park et al., 2012; Rahn & Wahlen, 1997; Toyoda et al., 2013; Yoshida & Matsuo, 1983; Yoshida & Toyoda, 2000). Long-term observation based on firn air from ice cores has revealed that the increase in the tropospheric $\text{N}_2\text{O}$ is mainly caused by the increase in anthropogenic emission (Intergovernmental Panel on Climate Change (IPCC), 2007; Ishijima et al., 2007). The primary anthropogenic emissions of $\text{N}_2\text{O}$ include agricultural soil and automobile exhaust. However, observation on isotopic ratios of $\text{N}_2\text{O}$ from six European stations (Kaiser et al., 2003) showed variability over several per mill confounding the attempt for flux estimation.

To better evaluate the anthropogenic contributions, it is important to monitor the $\text{N}_2\text{O}$ isotopic ratio variability over an urban/semi-urban station, which captures large anthropogenic emissions. In this regard, observations of $\text{N}_2\text{O}$ from Southeast Asian countries become important. Half the global population lives in the East Asia, including China and is experiencing rapid economic growth, confined mainly to urban areas. The urban growth of Asian countries leads to enhanced emission of $\text{N}_2\text{O}$. Thus monitoring from urban areas in this region will provide information on $\text{N}_2\text{O}$ emission from both natural and anthropogenic sources and its effect on the observed global tropospheric variability of $\text{N}_2\text{O}$. We have selected Taiwan, an island in the East Asia, located ~180 km away from the southeastern coast of China, that serves as an excellent monitoring station to analyze the seasonal variation of $\text{N}_2\text{O}$ isotopocules. This variation can be attributed mostly to differential contribution of its sources and sinks. We have further looked into the potential impact of air mass exchange between the lower stratosphere and upper troposphere in affecting the seasonal variability of $\text{N}_2\text{O}$ isotopocules in the lower troposphere.
2. Methods

2.1. Sampling Site

Air samples were collected during September 2013 to January 2016 normally at a daily frequency during weekdays from Academia Sinica (mentioned hereafter as "AS", (25°02′25″ N, 121°36′51″ E) campus in Taipei, Taiwan. In addition, during November 2011 to December 2014, samples were collected from Keelung (mentioned hereafter as "KL", (25°07′39″ N, 121°44′21″ E), a coastal station located northeast of Taipei. Taiwan has a subtropical climate strongly affected by monsoon systems throughout the year. During winter, Siberian high prevails in East Asia and extends toward the East China Sea as the winter monsoon progresses. This process transports air mass from northern China, passing over the industrial eastern China and picking up pollutants eventually reaching the northern part of Taiwan (Lin et al., 2004; Wang, 1974). In summer, it receives southwesterly/southeasterly winds, which carry oceanic air to the location (Araguás-Araguás & Froehlich, 1998; Peng et al., 2010). Both the coastal station KL and the inland station AS ought to monitor the seasonal air mass reversal and associated N₂O variability. Moreover, Taipei is located in a basin with mountains surrounding it, which allows trapping of polluted air in the low-lying boundary layer (particularly in winter) for an extended period (Seidel et al., 2010). We expect to see the signature of anthropogenically produced N₂O either from long range transport or from local sources. A detailed comparison of the Taipei values with that obtained at the nearest coastal station should delineate the local effects.

The sampling site at AS is located in the eastern side of Taipei city which falls into the zone of natural areas (Energy Synthesis 4, 2007) having significant N₂O emission from natural sources. These features make the sampling location at AS an ideal site to study the temporal variability of N₂O affected not only by natural and anthropogenic N₂O emission but also by synoptic weather conditions associated with the monsoon/subtropical jet systems.

In order to understand the physicochemical processes affecting the δ¹⁵N, δ¹⁸O, and SP values of N₂O at AS and Keelung (SP data could only be measured during October 2014 to December 2014), we compare our observations with that available from different stations with different atmospheric environment. For example, we try to relate our observation with the observation from a nearby island station, Hateruma (HAT; Toyoda et al., 2013) in Japan, which can be considered as a representative open ocean station (Figure 1). We also compare our observation with mid-tropospheric air N₂O data obtained as a part of the CARIBIC expedition (Laskar et al., 2019).
2.2. Air Sampling Details

2.2.1. Sampling Procedure

Air sampling was done at a height of ~10 m above ground inside the AS campus; at KL station sampling was done at ground level facing the open ocean. Sampling at both the sites was done mostly during the day (10:00–16:00 LST). Two samples were collected each time to check the integrity of sample collection, extraction, and isotopic analysis. Samples were collected using a diaphragm pump in two 1-liter Pyrex glass flasks (Francey et al., 1996) after passing through a magnesium perchlorate \([\text{Mg (ClO}_4\text{)}_2]\) trap to remove moisture. Prior to the collection, the entire assembly (Figure 2(a)) of flask and Mg (ClO\(_4\))\(_2\) trap and valves were flushed with the ambient air for 5 mins. Eventually the outlet stopcocks of the flasks were closed and the flasks were filled for ~10 min until a pressure of ~1.5 bar was obtained.

2.2.2. Extraction of N\(_2\)O From Air Sample

N\(_2\)O was cryogenically separated from the bulk air sample using a stainless steel extraction system (Figure 2(b)) equipped with U-traps and mass flow controller, whose vacuum was maintained by a rotary pump. The glass flask was connected at the entry port using an ultra-torr connector and the sample was extracted at a...
helium flow rate of 90 ml/min. At first all condensable gases were trapped in a U-trap (filled with glass beads) using liquid N$_2$ while non-condensable gases (like N$_2$, O$_2$, and Ar) were pumped out. Then the condensable gases like N$_2$O along with CO$_2$ were expanded into a 20 ml vial using needle for final mass spectrometric measurement, following the same protocol as described in the submission of our laboratory (identified as Lab #2) published in the inter-laboratory comparison report by Mohn et al. (2014).

2.2.3. Measurements of $\delta^{15}$N, $\delta^{18}$O, and SP

In our method, the extracted sample is introduced into an isotope ratio mass spectrometer (IRMS) Delta V-Plus (used since 2014), via a Conflow IV peripheral coupled with a pre-concentrator system with two traps (T1 and T2 as shown in Figure 2(c)) and an auto-sampler system, designed following Casciotti et al. (2002) but with some modifications. Before 2013 (2011–2012), samples from Keelung were analyzed by IRMS MAT 253 where site preference was not configured. The gas flow is controlled by an eight-port Valco valve as shown in Figure 2(c). In the Load mode (Figure 2c), He at a flow rate of 20 ml/min carries the gases from the sample vial and introduces it into the pre-con trap T1 at liquid nitrogen temperature. Prior to trapping in T1, the sample is passed through a Nafton drier and a chemical trap containing Mg (ClO$_4$)$_2$ and Ascarite packed alternately in sequence for removal of moisture and CO$_2$. Next, in the inject mode, He at a lower flow rate of 2 ml/min carries the N$_2$O from T1 to trap T2, and finally introduces it into a Gas Chromatograph (GC) equipped with an Agilent Poraplot Q column (25 m long, 0.32 mm i.d.) for further purification of N$_2$O from the residual CO$_2$ and other gases such as trace water (Tania et al., 2017). After GC separation, the purified N$_2$O enters the mass spectrometer via Conflow IV device. Both the bulk isotope ratios ($\delta^{15}$N, $\delta^{18}$O) and SP value of N$_2$O are measured simultaneously following standard protocol (Mohn et al., 2014). The nitrogen and oxygen isotopic ratios are reported relative to air N$_2$ and V-SMOW in ‰, respectively. The intramolecular distribution of $^{15}$N is determined via the ion beams of masses 30 and 31 as NO$^+$ species, i.e., $\delta$(31/30). Finally, the SP value of N$_2$O is determined following the equation: SP = $\delta^{15}$N$^{\alpha}$ – $\delta^{15}$N$^{\beta}$ (Toyoda & Yoshida, 1999), where $\delta^{15}$N$^{\alpha}$ and $\delta^{15}$N$^{\beta}$ values refer to the nitrogen isotopic compositions at the center and terminal positions, respectively, with the $\delta^{15}$N$^{\alpha}$ value determined by $\delta$(31/30). The bulk nitrogen isotope ratio, $\delta^{15}$N, is the average of $\delta^{15}$N$^{\alpha}$ and $\delta^{15}$N$^{\beta}$ values.

2.3. Standardization and Inter-Laboratory Calibration for N$_2$O

In our mass spectrometer, the sample N$_2$O is measured relative to a pure N$_2$O reference gas called Working Reference (mentioned hereafter as WR) which was calibrated via the “Tokyo Standard”, and the assigned values of $\delta^{15}$N and $\delta^{18}$O for WR are 3.46 ± 0.02 ‰ and 40.37 ± 0.05 ‰, respectively. As mentioned, we took part in an inter-laboratory calibration program (Mohn et al., 2014) where three N$_2$O cylinders, one with tropospheric isotopic concentration (synthetic air N$_2$O, called Target gas T) and two more cylinders of N$_2$O at ~90 μmol mol$^{-1}$ (named REF1 and REF2) with different $\delta^{15}$N, $\delta^{18}$O, and $\delta$(31/30) values, were circulated among different laboratories worldwide (see Mohn et al. (2014) for the description of the three gases). These were analyzed following the analytical protocol given in Mohn et al. (2014) where our laboratory is named as Lab#2 and the isotopic values were calculated using our WR as reference. Our values were close to the average values, certifying the validity of WR value assignments. However, when processing atmospheric N$_2$O samples, we found that the obtained $\delta^{15}$N, $\delta^{18}$O, and SP values were significantly different from the Hateruma samples reported by Toyoda et al. (2013). The differences possibly resulted from our extraction system, but the exact cause is not known. In an attempt to correct for the difference, we sent aliquots of air taken from our laboratory compressed air cylinder to Tokyo Institute of Technology, Japan for cross calibration and applied the corrections uniformly to the data. The derived isotopic corrections for $\delta^{15}$N, $\delta^{18}$O, SP were 0.7 ± 0.1, 0.4 ± 0.3, and −2.7 ± 0.4 ‰ respectively. These corrected data are presented in Figure 3.

In order to ensure the integrity of the mass spectrometric analysis over time and over a single batch of sample analysis, we obtained a cylinder with a nominal N$_2$O concentration of 20 μmol/mol which was used as a running reference (called RR) during air N$_2$O analysis. For its calibration, several aliquots of N$_2$O from RR (20 ml at room temperature and pressure, which gives comparable IRMS intensities as atmospheric N$_2$O samples) were analyzed along with the gases T, REF1 and REF2 mentioned above. Based on this data, we assigned $\delta^{15}$N = −1.4 ± 0.1 ‰, $\delta^{18}$O = 40.5 ± 0.2 ‰, and $\delta$(31/30) = 2.2 ± 0.2 ‰ to the RR cylinder gas. In our routine protocol, aliquots of N$_2$O from the RR cylinder are always analyzed along with air N$_2$O samples to identify any possible analytical problem and to calculate the raw isotopic ratios of the samples. The values of RR gas analyzed along with the samples are used to correct for analytical drifts in isotopic ratios.
during the day of analysis. The long-term reproducibility of single analysis based on aliquots of RR cylinder is 0.1 ‰ for δ¹⁵N, 0.1 ‰ for δ¹⁸O, and 0.3 ‰ for SP. As a routine practice, duplicate samples are analyzed at the same time and the mean differences between the pairs are found to be 0.1 ‰ for δ¹⁵N, 0.2 ‰ for δ¹⁸O, and 0.3 ‰ for SP. These values can be treated as the external reproducibility of the isotopic analyses. If the SP values between pairs differ by more than ~2‰ the data are not considered reliable and rejected (shown as dashed mark entries in the Supplementary Material 1 and 2).

Figure 3. The δ¹⁵N, δ¹⁸O, and SP values of atmospheric N₂O samples from the AS station plotted against dates (from September 2013 to January 2016) (gray symbols). The δ-values of samples collected from the coastal station KL (during part of the above period from October 2014 to December 2014) are shown by the purple symbols. Error bars refer to the difference between duplicate values.
2.4. Concentration Measurements

The N₂O concentration was also measured in a limited number of samples. For this, moisture-free air samples were collected in a 300 ml flask at a pressure of 2 bar. The mixing ratio was determined using the front cut method (Elkins et al., 1996; Hall et al., 2007) with a µ-ECD sensor on an Agilent Gas Chromatograph (model 6,890 N). The concentration scale was calibrated using three NOAA standards, with assigned concentrations of 313.14 nmol/mol, 330.38 nmol/mol, and 358.49 nmol/mol. In the current protocol, we were able to obtain a precision of ±1 nmol/mol. Based on analysis of air samples collected at the AS station during December 2014 and February 2015, the average mixing ratio (for a total of 20 samples) and the dispersion is 329 ± 3 nmol/mol. For technical reasons, the concentration analysis could not be done for all samples. The reason is, initially we did not have the GC and the NOAA tanks for calibration and we thought that mass spectrometer signal could be calibrated to derive the concentration. However, these data were not precise enough. Even after the GC installation, the calibration of the GC was not reliable initially. Later on, the GC was calibrated properly with NOAA cylinders and the concentrations could be determined accurately.

2.5. Meteorological Reanalysis

To understand the role of interactions between the boundary layer and upper level air masses on the analytical data, we use ERA-Interim reanalysis data (Dee et al., 2011) for the period of our observations. The zonal wind speed at 200 hPa is used to obtain the strength of the subtropical jet stream. To understand the effects of stratosphere–troposphere exchange on the station observation, meridional and vertical winds and Potential Vorticity (PV) values from the ERA-Interim reanalysis data obtained at 0.75° by 0.75° grid resolution are also analyzed on a daily scale. Vertical velocity (Pas)−1) is scaled by a factor −100. The factor −100 is used to make it consistent with the pressure scale (hPa) used in the study and the negative sign is used to retain the usual axis convention i.e. positive and negative values should mean rising and sinking motion of air respectively. PV is a measure of absolute circulation of an air parcel enclosed between the two isentropic surfaces and hence an indicator of static stability and air mass type (tropospheric/stratospheric) (Holton, 1992; Hoskins et al., 1985). The PV values are expressed in potential vorticity units or PVU (10−6 m−2 s−1 K kg−1). In the troposphere, PV values are usually low but they increase rapidly as one ascends to the stratosphere. The difference between daily value and the long-term (1979–2015) climatological daily mean was computed to find out the daily anomaly in the parameters and use them for stratospheric source identification.

3. Results and Discussions

3.1. Comparison With Other Available Observations

The values of δ¹⁵N, δ¹⁸O, and SP of N₂O samples obtained from the AS and KL stations (Supplementary Material 1 and 2) are plotted in Figure 3 as a function of time. (Data are archived at Harvard Dataverses https://doi.org/10.7910/DVN/RUWCHF.) The average δ¹⁵N value of the combined samples from the two stations is 6.4 ± 0.3 ‰. In general, the δ¹⁵N values are comparable to the average δ¹⁵N value of 6.6 ‰ expected for the year 2014 at Hateruma, obtained by extrapolation of data from Toyoda et al. (2013). Slightly lower values observed at AS and KL stations indicate contribution of isotopically depleted land emissions which are not significant at Hateruma. We also measured 21 whole air samples collected from upper levels of atmosphere (~10 km) in two CARIBIC flights from Düsseldorf to Isla Margarita and from Puerto Plata to Munich conducted in 2001–2002 (Laskar et al., 2019). The average δ¹⁵N value of these samples is 6.7 ± 0.1 ‰. Applying the observed annual trend for the period 2003–2010 as obtained from the HAT data, the average CARIBIC value should reduce to 6.5 ‰ in the year 2014. The δ¹⁸O values of our samples are comparable (with average of 44.0 ± 0.4 ‰ and 44.6 ± 0.4 ‰ for AS and KL respectively) to the values for HAT and CARIBIC samples with values of 44.2 ‰ and 44.0 ‰, respectively. The SP values of our N₂O samples are in general consistent with earlier studies. The mean value at AS is 17.1 ± 1.0 ‰ and that at KL is 17.9 ± 1.3 ‰.

Comparing our data with those of southern hemisphere clean air stations, we note that both AS and KL station have contribution from anthropogenic sources which can account for the observed difference. According to the trend given by Röckmann and Levin (2005), the values of δ¹⁵N and δ¹⁸O of N₂O for a clean southern hemisphere station in the year 2014 are expected to be ~6.4 ‰ and ~44.4 ‰, respectively.
Moreover, the variability in $\delta^{15}N$ and $\delta^{18}O$ values of N$_2$O is found to be larger when compared with other tropospheric stations; in European region, the variability was $\pm 0.12$‰ and $\pm 0.21$‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively (Kaiser et al., 2003).

3.2. Temporal Variation

Apart from the differences in isotopic ratios between the AS and KL, open ocean HAT, and upper air CARIBIC samples, there is a temporal variation in the data sets of both AS and KL samples. Both the $\delta^{15}N$ and $\delta^{18}O$ values were in general lower in summer than other seasons. The values increased slowly from October–November through core winter (December–February). For the KL station, the data is limited in 2011, but the temporal variation is clear in all other years. It is suspected that the seasonal reversal of wind system might be an important factor causing this variability. In winter, the wind is dominantly from the northern continents, whereas in summer the wind is from the South China Sea and Pacific Ocean side characterizing the monsoon system of Southeast Asia.

3.3. Anthropogenic Emissions

We discuss below the N$_2$O contribution from human activities using the nitrogen isotope tracer, for the aforementioned isotopic depletion in summer. As mentioned above, the mean N$_2$O concentration measured at AS is $329 \pm 3$ nmol/mol (Supplementary Material 3; https://doi.org/10.7910/DVN/RUWCHF). This value is $3 \pm 3$ nmol/mol higher than the HAT value for the year 2014 (applying a trend of $0.7$ nmol/mol yr$^{-1}$ to the concentration value of the year 2010 for which the data is available), whereas the average $\delta^{15}N$ value at AS ($6.4 \pm 0.3$‰) is $0.2$‰ lower that HAT. Assuming that the values at Hateruma represent the regional background ($\delta^{15}N_b$ and [N$_2$O]$_b$), the anthropogenic contribution to the N$_2$O at AS station can be estimated by a simple mass balance,

$$\Delta [N_2O] = (\delta^{15}N_b - \delta^{15}N) / (\delta^{15}N_b - \delta^{15}N_{anth}) \times [N_2O]_b$$

To explain the reduction of $0.2$‰ in $\delta^{15}N$ (relative to $\delta^{15}N_b$) with $\Delta [N_2O] = 3$ nmol/mol requires $\delta^{15}N_{anth}$ as low as $-15$‰, a value which can be natural or agricultural soil emission (Park et al., 2012; Pérez et al., 2000, 2001; Rock et al., 2007; Toyoda et al., 2011). However, extensive regional N$_2$O measurements are needed, in order to determine accurately the source region(s) of the depleted N$_2$O.

3.4. Enhanced Stratosphere-Troposphere Exchange

Interestingly, at Taipei station, enhancements in $\delta^{15}N$, $\delta^{18}O$, and SP values are observed in winter (Figure 4), concurrent with the enhancement of zonal wind anomaly. It is seen that the weekly averaged $\delta^{15}N$, $\delta^{18}O$, and SP values of N$_2$O and zonal wind anomaly both increase during October–December. A Monte Carlo based bootstrapping analysis (Efron & Tibshirani, 1993) using a set of 1,000 repeated re-samplings for the dataset was applied first, followed by a weekly averaged method to the prescribed weekly bins (Sunday–Saturday) to determine the trends in the isotopic ratios. The trends for the AS station are found to be $0.006 \pm 0.002$‰/day, $0.010 \pm 0.002$‰/day, and $0.008 \pm 0.002$‰/day for $\delta^{15}N$, $\delta^{18}O$, and SP, respectively, concordant with the strengthening of the subtropical jet stream (indicated by enhancement in weekly averaged 200 hPa zonal wind speed) during the same period. Similar to AS station, positive trends in $\delta^{15}N$ ($0.013 \pm 0.005$‰/day), $\delta^{18}O$ ($0.011 \pm 0.005$‰/day) and SP ($0.011 \pm 0.027$‰/day) are also found at KL station. Trend, though weaker, is also seen during October 2015 to December 2015 over AS station. The positive trend in all isotopocules in these two stations is indicative of a common cause. We suspect that deep stratospheric incursion carrying enhanced isotopic signatures to this region took place during the aforementioned period. The phenomenon of stratospheric incursion in this region associated with subtropical jet stream was also noted earlier by Liang and Mahata (2015) and Lin, Su, et al., 2016, Lin, Zhang, et al., 2016). However, we cannot rule out the possibility that the summer–fall reduction in N$_2$O isotopic ratios could be due to elevated local/regional sources of N$_2$O with decreasing strength toward the end of the year. This latter mechanism requires that there exist sources where N$_2$O isotopocules ($\delta^{15}N$, $\delta^{18}O$, and SP) are depleted by similar magnitude compared to the mean tropospheric isotope values and emit at variable magnitudes following the enhancement of the jet stream, but such sources have not been reported. The observed trend could also be caused by a combination of the above two processes. At this moment, stratospheric incursion is the most likely source of the variability, as the reported relative...
Fractionation factors between $^{15}$N, $^{18}$O, and SP are consistent with model predictions (Kaiser et al., 2006; McLinden et al., 2003; Morgan et al., 2004; Toyoda et al., 2013). Possibility of stratospheric incursions is further investigated based on vorticity and wind motions in Figure 5. There are several episodes where air parcels with elevated PV values are seen reaching mid-to-upper troposphere from the lower stratosphere (100 hPa and above). Since the troposphere is thermodynamically unstable, air reaching mid-to-upper troposphere is mixed with the unstable lower tropospheric column by the sinking/rising branch of meridional circulation and by the local updrafts/downdrafts (Stohl et al., 2003). Thus, a surface station might be able to record signature of stratospheric intrusion. Over our station, we notice episodes of anomalous rising/subsidence of combined meridional and vertical wind (vertical velocity is scaled by a factor of $-100$; for better visualization, the vectors are shown at alternate pressure levels). Also shown in the background is daily local vertical velocity (scaled by a factor of $-100$; color shaded). These sinking motions (shown by arrows) combined with the local downdrafts can bring the air further down in the troposphere. In the lower tropospheric levels, boundary layer processes are prominent, and enhanced turbulent mixing can further transport the air masses to ground levels. Similar observations in tropospheric ozone variability are also reported from an urban site in Kawsara, Senegal, West Africa (Hu et al., 2010). We looked for a correlation of isotope ratios with the potential vorticity values at the ground level, but since the isotope ratios are influenced by several factors at the lower level, a one-to-one correlation is not observed.

3.5. Connection With Oxygen Isotope Anomaly in CO$_2$

It is known that stratospheric processes not only increase $\delta^{15}$N and $\delta^{18}$O values of N$_2$O but also enhance the oxygen isotope anomaly ($\Delta^{17}$O) in CO$_2$ (Boering et al., 2004; Liang & Mahata, 2015). The stratospheric
signals carried downward by air mass incursions are diluted by terrestrial processes. As a result, one may use the level of the residual stratospheric signal to deduce the biogeochemical fluxes of N$_2$O at the surface (Kaiser et al., 2006; McLinden et al., 2003; Morgan et al., 2004; Park et al., 2012; Toyoda et al., 2013), similar to what was done using CO$_2$ isotope anomaly (Laskar et al., 2019; Liang, Mahata, Laskar, Thiemens, & Newman, 2017). The stratospheric N$_2$O is characteristically different from other terrestrial sources of N$_2$O, being highly enriched in oxygen isotope ratio. A downward incursion of stratospheric air mass carrying N$_2$O, as suggested by an increase in 200 hPa zonal wind speed in 2014 winter near Taiwan (Figure 4), can enhance the isotopic ratio as observed at AS station. However, such phenomenon is likely to be local, as no evidence of stratospheric intrusion is seen at HAT. Therefore, to utilize the unique stratospheric signals in N$_2$O for determining its biogeochemical flux at the surface requires a model with horizontal resolution at least ~1° × 1° (the distance between Taiwan and HAT is ~200 km), in order to resolve this local feature. We will defer this to a future study.

Based on a scaling of CO$_2$ anomalies using zonal wind, we can make a simple quantitative estimate of enrichment. The oxygen isotope anomaly of CO$_2$ in the downwelling branch from the stratosphere is about 1 ‰ (0.5 to 1.0 ‰ as per CARIBIC paper, Laskar et al., 2019) higher than that of the tropospheric CO$_2$ (Hofmann et al., 2017; Liang, Mahata, Laskar, & Bhattacharya, 2017; Liang & Mahata, 2015; Liang, Mahata, Laskar, Thiemens, & Newman, 2017; Thiemens et al., 2014). The observed oxygen anomaly trend in CO$_2$ in October–November, 2013 is ~0.1 ‰/month while the trend for the 200 hPa zonal wind is ~25 m/s/month (taken from Liang & Mahata, 2015). The good correlation between the oxygen anomaly and 200 hPa zonal winds allows one to use the zonal wind change for the estimation of downwelling flux of δ$_{15}^{15}$N from the stratosphere. In October–November, 2014, the 200 hPa zonal wind change is estimated to be ~17 m/s/month, implying an expected trend of 0.07 ‰/month in the oxygen anomaly in CO$_2$. The δ$_{15}^{15}$N, δ$_{18}^{18}$O, and SP values of N$_2$O from the stratosphere are estimated to be ~3 ‰ above the tropospheric values (Liang & Yung, 2007; Morgan et al., 2004; Toyoda et al., 2013), a factor of 3 higher than that of the oxygen anomaly (Δ$^{17}$O) in stratospheric CO$_2$. This means that the trend in δ$_{15}^{15}$N, δ$_{18}^{18}$O, or SP expected from the change of the zonal wind should be ~0.2 ‰/month in N$_2$O, close to the observed trend of ~0.3 ‰/month (Figure 4). This comparison qualitatively supports the hypothesis that the elevation of N$_2$O isotopocules during the period of subtropical jet-strengthening is of stratospheric origin.
4. Conclusion

The isotopic ratios of nitrogen and oxygen in atmospheric N$_2$O samples obtained from two places in Taiwan, Academia Sinica (AS) in Taipei and Keelung (KL) coastal town (an urban habitat and a coastal region respectively) located in the west Pacific region have been measured. Depleted isotope ratios were found for the AS and KL stations compared to the values from an open ocean station at Hateruma (HAT) or from upper air samples (from CARIBIC mission). Such depletion could be caused by enhanced contribution from anthropogenically emitted N$_2$O from local sources (which has lower oxygen and nitrogen isotopic ratios). Over and above this depletion, there is a strong temporal variability in the three isotopic parameters, $\delta^{15}$N, $\delta^{18}$O, and SP values of N$_2$O, observed for both the AS and the KL station. In addition, steady enhancement in $\delta^{15}$N, $\delta^{18}$O, and SP values is seen during the subtropical jet-strengthening period in wintertime. We suspect that this is due to occasional and variable incursion of upper tropospheric/lower stratospheric air masses carrying N$_2$O in this region, which is enriched in isotope ratios. This hypothesis is supported by the observed increase in upper air zonal wind speed, linked to enhanced vertical transport and also by the enhancements of the $\Delta^{17}$O values in CO$_2$ (Liang & Mahata, 2015) and $^{35}$S activity in atmospheric sulfate aerosols (Lin, Su, et al., 2016; Lin, Zhang, et al., 2016) during the winter season. With the stratospheric signals distinct from that at lower troposphere which originates at the surface, we expect that the utilization of multiple isotopic tracers ($\delta^{15}$N/$\delta^{18}$O/SP of N$_2$O and $\Delta^{17}O$ of CO$_2$) can provide a strong constraint for local emissions from the surface, improving our knowledge of the emission fluxes of N$_2$O.

References

Araguás-Araguás, L., & Froehlich, C. (1998). Stable isotope composition of precipitation over southeast Asia. Journal of Geophysical Research, 103(D22), 28,721–28,742. https://doi.org/10.1029/98JD02582

Boering, K. A., Jackson, T., Hoag, K. J., Cole, A. S., Perri, M. J., Thiemen, M., & Atlas, E. (2004). Observations of the anomalous oxygen isotopic composition of carbon dioxide in the lower stratosphere and the flux of the anomaly to the troposphere. Geophysical Research Letters, 31, L03109. https://doi.org/10.1029/2003GL018451

Casatti, K. L., Sigman, D. M., Galanter Hastings, M., Böhlke, J. K., & Hilbert, A. (2002). Measurement of the oxygen isotopic composition of nitrate in marine and fresh waters using the densitometric method. Analytical Chemistry, 74(19), 4905–4912. https://doi.org/10.1021/ac02013w

Cliff, S. S., & Thiemen, M. H. (1997). The $^{18}$O/$^{16}$O and $^{17}$O/$^{16}$O ratios in atmospheric nitrous oxide: A mass-independent anomaly. Science, 278(5344), 1774–1776. https://doi.org/10.1126/science.278.5344.1774

Crutzen, P. J., & Quay, J. R. (1970). The influence of nitrogen oxides on the atmospheric ozone content. Meteorological Society, 96(408), 320–325. https://doi.org/10.1002/qj.49709640815

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., et al. (2011). The ERA-interim reanalysis: Configuration and performance of the data assimilation system. Quarterly Journal of the Royal Meteorological Society, 137(655), 553–597. https://doi.org/10.1002/qj.828

Elfvin, B., & Tibshirani, R. (1993). An Introduction to the Bootstrap. New York: Chapman & Hall/CRC.

Elkins, J. W., Fahey, D. W., Gilligan, J. M., Dutton, G. S., Baring, T. J., Volk, C. M., et al. (1996). Airborne gas chromatograph for in situ measurement of long-lived species in the upper troposphere and lower stratosphere. Geophysical Research Letters, 23, 347–350.

Franczy, R. J., Steele, L. P., Langenfelds, R. L., Lucarelli, M. P., Allison, C. E., Broderick, D. J., et al. (1996). Global Atmospheric Sampling Laboratory (GASLAB): Supporting and extending the Cape Grim trace gas programs. In R. J. Francey, A. L. Dick, & N. Derek (Eds.), Baseline Atmospheric Program Australia (Australia) 1993 (pp. 8–29). Melbourne: Department of the Environment, Sport and Territories, Bureau of Meteorology in Cooperation with CSIRO Division of Atmospheric Research.

Graven, H. D., Keeling, R. F., Piper, S. C., Patra, P. K., Stephens, B. B., Wofsy, S. C., et al. (2013). Enhanced seasonal exchange of CO$_2$ by northern ecosystems since 1960. Science, 341(6150), 1085–1089. https://doi.org/10.1126/science.1239207

Hall, B. D., Dutton, G. S., & Elkins, J. W. (2007). The NOAA nitrous oxide standard scale of atmospheric observations. Journal of Geophysical Research, 112, D19305. https://doi.org/10.1029/2006JD007954

Hofmann, M. E. G., Horváth, B., Schneider, L., Peters, W., Schützenmeister, K., & Andreas, P. (2017). Atmospheric measurements of $\Delta^{17}$O in CO$_2$ in Göttingen, Germany reveal a seasonal cycle driven by biospheric uptake. Geochimica et Cosmochimica Acta, 199, 143–163. https://doi.org/10.1016/j.gca.2016.11.019

Holton, J. R. (1992). Introduction to Dynamic Meteorology. New York: Elsevier.

Hoskins, B. J., McIntyre, M. E., & Robertson, A. W. (1985). On the use and significance of isentropic potential vorticity maps. Quarterly Journal of the Royal Meteorological Society, 111(470), 877–946. https://doi.org/10.1002/qj.4711147002

Hu, X. M., Fuentes, J. D., & Zhang, F. (2010). Downward transport and modification of tropospheric ozone through moist convection. Journal of Atmospheric Chemistry, 65(1), 13–35. https://doi.org/10.1007/s10874-010-9179-5

Intergovernmental Panel on Climate Change (IPCC) (2007). In S. Solomon, et al. (Eds.), Climate Change 2007: The Scientific Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. New York: Cambridge Univ. Press.

Intergovernmental Panel on Climate Change (IPCC) (2001). In J. T. Houghton, et al. (Eds.), Climate Change 2001: The Scientific Basis: Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change (p. 881). New York: Cambridge Univ. Press.

Ishijima, K., Sugawara, S., Kawamura, K., Hashida, G., Morimoto, S., Murayama, S., et al. (2007). Temporal variations of the atmospheric nitrous oxide concentration and its $\delta^{14}$N and $\delta^{15}$O for the latter half of the 20th century reconstructed from firn air analyses. Journal of Geophysical Research, 112, D03305. https://doi.org/10.1029/2006JD007208
