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N_2O as a tracer of mixing stratospheric and tropospheric air based on CARIBIC data with applications for CO_2

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HIGHLIGHTS

- We explore the concept to use N_2O as another STE tracer for trace-gases in UTLS.
- We analyze the distribution of de-trended N_2O for NH ground stations and UTLS region.
- We introduce the N_2O-threshold aimed to distinguish tropospheric and stratosphere-affected air.
- We demonstrate the use of N_2O as a STE tracer for CO_2 and CO_2 isotopes in UTLS.
- We demonstrate the use of N_2O as a tracer for STE flux by deep stratospheric intrusions.

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ABSTRACT

Stratosphere–troposphere exchange (STE) affects distributions of trace gases, with ozone (O_3) and CO being commonly used to study mixing process in the UTLS (Upper Troposphere and Lower Stratosphere) region. Here we explore the application of N_2O as a tracer of stratosphere to troposphere flux for CO_2 and its isotopes, using N_2O and CO_2 mixing ratios including a set of CO_2 isotope data for CARIBIC aircraft samples and NOAA-Carbon Cycle flask samples. A frequency distribution of CARIBIC N_2O data (mostly UTLS at mid- and high-latitudes) reveals a narrow distribution around a tropospheric maximum at nearly the same N_2O mixing ratio as the distribution peak for the station Mauna Loa (MLO) however with a skewing due to STE. We demonstrate that upper-tropospheric and STE-affected air can be distinguished using a threshold value based on the N_2O distribution width at MLO. A comparison with the use of O_3 is given. N_2O is discussed to be a robust and linear (season and latitude independent) tracer of STE mixing proportions. We propose that CARIBIC data coupled with CO_2 isotopic data published for the stratosphere and data of NOAA stations can be used as a frame of reference for $\delta^{18}O(CO_2)$ and $\Delta^{17}O(CO_2)$ STE fluxes. The $\Delta^{17}O(CO_2)$ flux is of particular interest as it is thought to constrain estimates of biosphere productivity, atmospheric oxygen cycle and global gross CO_2 fluxes. CARBIC data can also help tracing STE flux by deep stratospheric intrusions and a data analysis is given for the Walliguan (WLG) observatory on the Tibetan Plateau.

1. Introduction

Stratosphere/Troposphere Exchange (STE) has been studied especially because of its importance for the flux of O_3 into the troposphere. The net downward flux likewise delivers air with specific stratospheric “signatures”, e.g. a depletion in N_2O, causing detectable reductions in upper tropospheric N_2O mixing ratios (e.g. (Ishijima et al., 2010)). Similarly the tropospheric distributions of other important trace gases, especially CO_2 and CH_4 are affected by the stratosphere to troposphere flux, with the net effect depending on the air mass fluxes and growth rate (e.g. SF_6), or growth rate and seasonality (e.g. CO_2) or growth rate, seasonality, and chemistry (e.g. N_2O and CH_4).

Most experimental STE investigations are based on correlations between O_3 and CO measured onboard research aircraft, whereby O_3 is the tracer for stratospheric air and CO for tropospheric air.

Abbreviations: UTLS, Upper Troposphere and Lower Stratosphere; LMS, Lower Most Stratosphere; O_3-CT, Ozone-Chemical Tropopause defined after (Zahn et al., 2004a); STE, Stratosphere–Troposphere Exchange; PV, Potential Vorticity; PVU, Potential Vorticity Units.

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Detailed analysis of CO–O_3 correlations (e.g. (Hoor et al., 2004; Pan et al., 2004; Zahn et al., 2004a,b)) have highlighted the complexity of mixing in the UTLS and revealed the existence of a variable mixing layer in the Lowermost Stratosphere (LMS). In such studies the use of parameters measured onboard is preferred over the use of Potential Vorticity (PV) values as derived from the re-analyses of meteorological model data, because of the higher spatial resolution of the experimental data. Moreover, a selection of in situ measured tracers is often available.

For all flights of CARIBIC, ~50% of the time is spent in the LMS with the balance in the troposphere. For a total of 3600 samples since 2005, 47% pertain to PV values of 1.5 PVU or higher and 33% was sampled in air masses having PV values of over 3.5. This choice for discriminating stratospheric air from tropospheric air is to a degree arbitrary and in this paper we will scrutinize the use of the distribution of N_2O in the UTLS. The accidental coincidence that large passenger aircraft cruise most efficiently exactly there where the tropopause forms at mid-latitudes, there where in the northern hemisphere (NH) most air traffic takes place due to economical developments, thus intersecting the tropopause frequently, render passenger aircraft measurements especially useful for STE studies insofar the relevant parameters can be measured using such platforms.

N_2O, with a lifetime of ~120 years, has a near uniform distribution in the troposphere, with little seasonal variation and is only removed in the stratosphere (Nevison et al., 2011, 2004) and references therein. The immediate reason for exploring N_2O is that the CARIBIC observatory (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, www.caribic-atmospheric.com) has generated fairly large sets of trace gas data, including N_2O, using air samples collected. For a subset of CARIBIC flights CO_2 isotopes have been measured (Assonov et al., 2009).

One question dealt with in this paper targets the measurement precision required for a given STE tracer. One can question if it is necessary to improve measurement precisions of O_3, CO_2, N_2O, CH_4, or SF_6 to optimize the information we gain. Related are questions pertaining to spatial and time resolution as well as the inter-seasonal comparability of the tracer. Although often practical considerations like availability of equipment is decisive, it stands to reason to analyze the performance of tracers for certain processes, particularly since passenger aircraft will continue to be used in the years to come (e.g. (Brenninkmeijer and CARIBIC-Team, 2007; Cammas and Volz-Thomas, 2007; Machida et al., 2007; Volz-Thomas and IAGOS-Team, 2007)).

Besides the development of the use of passenger aircraft, high performance optical analyzers for in situ measurement of CO_2, CH_4, N_2O and CO have become available. Since N_2O is an important greenhouse gases with a complex budget and therefore will be measured more frequently, it is worthwhile to explore what scope N_2O measurements in the UTLS have. Although N_2O data is still based on post flight flask analyses in many laboratories and thus suffers the disadvantage of a smaller dataset with relatively lower resolution compared to O_3, this situation will change to warrant a closer look. The CARIBIC N_2O dataset is currently one of the largest ones in the UTLS region. In conjunction with CO_2, N_2O may have advantages over the use of the much shorter lived O_3, and here we follow up the approach discussed by Assonov et al. (2010). The other data set we use is for N_2O results of flask sampling obtained for stations by the National Oceanic and Atmospheric Administration-Earth System Research Laboratory (NOAA-ESRL).

Here we also focus on CO_2 and CO_2 oxygen isotope signals in the UTLS (Upper Troposphere/Lower Stratosphere) using N_2O as a tracer. For improved understanding of the carbon cycle and to "constrain" carbon fluxes, tropospheric CO_2 concentrations are widely measured. In addition, isotopic analyses are used to shed additional light on the carbon cycle, with $\delta^{18}O$ being mostly controlled by the atmosphere-land biosphere CO_2 exchange e.g. (Welp et al., 2011). In the stratosphere however, $\delta^{17}O$–$\delta^{18}O$ of CO_2 is modified by photochemistry, namely through its interaction with $O(^1D)$ formed through the photolysis of O_3 under energetic UV light (Yung et al., 1991). Given the highly unusual oxygen isotopic composition of stratospheric O_3 (Heidenreich and Thiemens, 1983; Mauersberger, 1981), namely a strong enrichment in ^{18}O and especially a disproportionally high enrichment in ^{17}O, stratospheric CO_2 bears a unique signal that in its origin fundamentally differs from all isotope signals due to tropospheric processes. The ST (Stratosphere–Troposphere) flux delivers such specifically isotopically modified CO_2 to the troposphere. Moreover, the global flux of excess $^{17}O(CO_2)$ to the troposphere is a special tracer that helps to evaluate global biosphere productivity and global CO_2 fluxes (Hoag et al., 2005; Luz et al., 1999).

In the following sections we will analyze the N_2O frequency distributions at the NH background stations and in the UTLS obtained by CARIBIC. This demonstrates that tropospheric and STE-affected air can be distinguished using a certain threshold of the N_2O mixing ratio. Then we compare resolving ability of O_3 and N_2O for STE events and discuss differences in tracer seasonality including UTLS at mid- and high-latitudes and the Polar Vortex. Moreover, to verify the applicability of the N_2O-based approach, we investigate CO_2 isotope data obtained previously by aircraft, balloon and surface measurements. The use of N_2O is evaluated to constrain flux estimates of excess ^{17}O and ^{18}O in CO_2 into the troposphere. Finally we discuss how stratospheric signals in N_2O, $^{17}O(CO_2)$ and $^{18}O(CO_2)$ can be distinguished during deep stratospheric intrusions.

2. Data analysis

2.1. NOAA N_2O data and de-trending

The NOAA-ESRL N_2O data provide a representative geographical and seasonal coverage (Hall et al., 2007). A description of data and analytical aspects is given by Hirsch et al. (2006). N_2O was analyzed for the same flask samples that were also used for CO_2 and its isotope measurements.

The N_2O time series for Mauna Loa, Hawaii (MLO), Barrow, Alaska (BRW) and South Pole Observatory, Antarctica (SPO) (Fig. 1, Table 1) demonstrate the four key features of the global N_2O distribution: the monotonous increase, weak seasonal cycles with a NH–SH ~180° phase shift and a small NH–SH gradient. Stations in the higher NH latitudes capture the larger seasonality with a peak-to peak amplitude of ~2.2 ppb. It was concluded that stratospheric influx of low N_2O air is one of two major drivers of the N_2O seasonality at high latitudes (Nevison et al., 2011), the second one is the ocean degassing.

For de-trending N_2O data we use the increase rate observed at MLO. The linear fit for the MLO data (Jan-2007–Dec-2011, 0.844 ± 0.001 ppb y^{-1}, Fig. 1, upper panel) captures nearly all of the variance with residuals being symmetrically distributed with a standard deviation of 0.33 ppb (1σ). Because the precision of CARIBIC data is 0.35 ppb (1σ), we do not apply a sine-function to account for N_2O seasonality, which is about 1.3 ppb from peak to peak at MLO with significant interannual variability. Another potential complication not considered here is a small interannual variability in the N_2O rate of increase (Nevison et al., 2011). However, a refined de-trending is not needed for the present application; the MLO peak width of 0.33 ppb includes seasonal and interannual variability as well as the analytical uncertainty.

Because N_2O at background NH stations confirms the absence of a latitudinal gradient and demonstrate the same rate of increase (cf. Table 1 and Fig. 1), the same de-trending is applied to data from all