TransCom \(\text{N}_2\text{O}\) model inter-comparison – Part 1: Assessing the influence of transport and surface fluxes on tropospheric \(\text{N}_2\text{O}\) variability

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Abstract. We present a comparison of chemistry-transport models (TransCom-\(\text{N}_2\text{O}\)) to examine the importance of atmospheric transport and surface fluxes on the variability of \(\text{N}_2\text{O}\) mixing ratios in the troposphere. Six different models and two model variants participated in the inter-comparison and simulations were made for the period 2006 to 2009. In addition to \(\text{N}_2\text{O}\), simulations of CFC-12 and \(\text{SF}_6\) were made by a subset of four of the models to provide information on the models’ proficiency in stratosphere–troposphere exchange (STE) and meridional transport, respectively. The same prior emissions were used by all models to restrict differences among models to transport and chemistry alone. Four different \(\text{N}_2\text{O}\) flux scenarios totalling between 14 and 17 TgN yr\(^{-1}\) (for 2005) globally were also compared. The modelled \(\text{N}_2\text{O}\) mixing ratios were assessed against observations from in situ stations, discrete air sampling networks and aircraft. All models adequately captured the large-scale patterns of \(\text{N}_2\text{O}\) and the vertical gradient from the troposphere to the stratosphere and most models also adequately captured the \(\text{N}_2\text{O}\) tropospheric growth rate. However, all models underestimated the inter-hemispheric \(\text{N}_2\text{O}\) gradient by at least 0.33 parts per billion (ppb), equivalent to 1.5 TgN, which, even after accounting for an overestimate of emissions in the Southern Ocean of circa 1.0 TgN, points to a likely underestimate of the Northern Hemisphere source by up to 0.5 TgN and/or an overestimate of STE in the Northern Hemisphere. Comparison with aircraft data reveal that the models overestimate the amplitude of the \(\text{N}_2\text{O}\) seasonal cycle at Hawaii (21° N, 158° W) below circa 6000 m, suggesting an overestimate of the importance of stratosphere to troposphere transport in the lower troposphere at this latitude. In the Northern Hemisphere, most of the models that provided CFC-12 simulations captured the phase of the CFC-12, seasonal cycle, indicating a reasonable representation of the timing of

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STE. However, for N$_2$O all models simulated a too early minimum by 2 to 3 months owing to errors in the seasonal cycle in the prior soil emissions, which was not adequately represented by the terrestrial biosphere model. In the Southern Hemisphere, most models failed to capture the N$_2$O and CFC-12 seasonality at Cape Grim, Tasmania, and all failed at the South Pole, whereas for SF$_6$, all models could capture the seasonality at all sites, suggesting that there are large errors in modelled vertical transport in high southern latitudes.

N$_2$O emissions can be estimated from atmospheric observations with the use of an atmospheric chemistry transport model (CTM) to translate between concentrations and fluxes. This is formalized in atmospheric inversions, where the estimated fluxes are those that provide the best fit to the observations while remaining within the bounds of the prior flux estimate and the assigned uncertainties. However, extracting information about N$_2$O fluxes from atmospheric observations is extremely challenging owing to the small signal-to-noise ratio of these measurements. For instance, the typical precision on a discrete air sample is about 0.3 ppb while the annual mean inter-hemispheric gradient is 1.4 ppb. In addition, there are complications of atmospheric transport, in particular, STE (Nevison et al., 2011). This is one of the main motivations for this study, i.e. to investigate what can be learnt from atmospheric measurements of N$_2$O and to what extent these can advance knowledge about surface fluxes. Simulations of N$_2$O using CTMs can help our understanding of the influence of transport on N$_2$O spatial and temporal variability. Ultimately though, our knowledge about N$_2$O emissions through atmospheric inversions will only improve with a quantification of the uncertainties in modelled atmospheric transport and in the prior emissions.

TransCom is a community that was established in the early 1990s primarily to examine the performance of CTMs. Early studies included verification of transport using the anthropogenic tracer SF$_6$ (Denning et al., 1999) and examining simulations of atmospheric CO$_2$ (Law et al., 1996; Law et al., 2008). More recently, there was a TransCom study to investigate the roles of emissions, transport and chemical loss on CH$_4$ (Patra et al., 2011). In this TransCom study, we examine the influence of emissions, tropospheric transport and STE on the variability in atmospheric N$_2$O. In particular, we focus on annual to seasonal timescales. Additionally, we aim to assess the influence of atmospheric transport errors on modelled N$_2$O concentrations, which are used in the interpretation of inverse modelling results for N$_2$O emissions (discussed in a companion paper: Thompson et al. 2014b). Six different models and two model variants are included in this forward inter-comparison study and five atmospheric inversion models are included in the inversion study.

In Sect. 2, we describe the atmospheric observations used in the inter-comparison and give details about the models that participated in this study as well as about the study’s protocol. Following this, in Sect. 3.1, we present the inter-comparison of large-scale transport features such as the inter-hemispheric (IH) gradient and cross-tropopause gradient. In Sect. 3.2, we examine the tropospheric N$_2$O seasonal cycle and use comparisons with SF$_6$ and CFC-12 to help disentangle the contributions from STE, tropospheric transport and surface emissions on N$_2$O concentrations. CFC-12 has been previously used as a tracer for STE (Nevison et al., 2007) as it has comparatively well-known emissions, which have little seasonal variability but, like N$_2$O, it is only lost in the stratosphere. SF$_6$ is a useful tracer for tropospheric transport,
as it also has comparatively well-known emissions, which are largely in the Northern Hemisphere (NH) and it can be treated as inert since it has an estimated lifetime of between 800 and 3200 years (Morris et al., 1995; Ravishankara et al., 1993). Lastly, in Sect. 4, we discuss what can be learnt about N₂O emissions from model–observation comparisons and the implications of atmospheric transport uncertainties for N₂O emission estimates from inversions.

2 Observations, models and methods

2.1 Modelling protocol

A schematic overview of the modelling protocol is shown in Fig. 1 with the different components of the model set-up. To facilitate the analysis of the results in terms of atmospheric transport, all modelling groups were requested to use the same prior fluxes (for N₂O, SF₆ and CFC-12) and the same magnitude for the stratospheric sinks of N₂O and CFC-12. On the other hand, each transport model was used with its own meteorological analysis data or, alternatively, meteorological fields nudged to analysis data in offline atmospheric transport runs (see Table 1). Since each transport model has different vertical and horizontal resolution, each model was also used with its own initial 3-D mixing ratio fields.

For simulations of N₂O, it was necessary to account for the loss of N₂O in the stratosphere due to photolysis (circa 90% of the loss) and oxidation by O(¹D) (circa 10% of the loss) (Minschwaner et al., 1993). These processes can be summarized by the following three equations:

\[ \text{N}_2\text{O} \xrightarrow{hv} \text{N}_2 + \text{O}^1\text{D} \]  
\[ \text{N}_2\text{O} + \text{O}^1\text{D} \xrightarrow{k_1} 2\text{NO} \]  
\[ \text{N}_2\text{O} + \text{O}^1\text{D} \xrightarrow{k_2} \text{N}_2 + \text{O}_2 \]

Losses of N₂O were calculated on the basis of these equations within each CTM for every grid cell and time step. Although the exact photolysis and oxidation rates varied between models, these were scaled such that the global annual total loss of N₂O was approximately 12.5 TgN, consistent with estimates of the atmospheric abundance and the lifetime of N₂O, which is estimated to be between 124 and 130 years (Prather et al., 2012; Volk et al., 1997). Similarly, for models participating in the CFC-12 inter-comparison, it was necessary to account for photolysis of CFC-12 in the stratosphere (R4), which accounts for 93 to 97% of the total loss (Seinfeld and Pandis, 1998). This was done in the same way as for N₂O — that is, the photolysis rates were scaled to be consistent with a CFC-12 lifetime of circa 100 years:

\[ \text{CF}_2\text{Cl}_2 \xrightarrow{hv} \text{CFCl} + \text{Cl}^- \]  

Model simulations were made using meteorology and surface emissions for the period from 1 January 2005 to 31 December 2009, with 2005 being considered as a “spin-up” year.
Table 2. Overview of the reference prior fluxes (OCNPIC) (totals shown for 2005).

| Category                                      | Data set          | Resolution | Total (TgN yr\(^{-1}\)) |
|-----------------------------------------------|-------------------|------------|--------------------------|
| Terrestrial biosphere                         | ORCHIDEE O-CN     | monthly    | 10.83                    |
| Ocean                                         | PISCES            | monthly    | 4.28                     |
| Waste water                                   | EDGAR-4.1         | annual     | 0.21                     |
| Solid waste                                   | EDGAR-4.1         | annual     | 0.004                    |
| Solvents                                      | EDGAR-4.1         | annual     | 0.05                     |
| Fuel production                               | EDGAR-4.1         | annual     | 0.003                    |
| Ground transport                              | EDGAR-4.1         | annual     | 0.18                     |
| Industry combustion                           | EDGAR-4.1         | annual     | 0.41                     |
| Residential & other combustion                | EDGAR-4.1         | annual     | 0.18                     |
| Shipping                                      | EDGAR-4.1         | annual     | 0.002                    |
| Other sources                                 | EDGAR-4.1         | annual     | 0.0005                   |
| Biomass burning                               | GFED-2            | monthly    | 0.71                     |
| Total                                         |                   |            | 16.84                    |

Table 3. Overview of the additional prior fluxes (totals shown for 2005).

| Flux set     | Categories                                      | Data set          | Resolution | Total (TgN yr\(^{-1}\)) |
|--------------|-------------------------------------------------|-------------------|------------|--------------------------|
| OCNN95       | terrestrial biosphere                           | ORCHIDEE OCN      | monthly    | 10.83                    |
|              | ocean                                           | Nevison et al. 1995 | monthly | 3.59                     |
|              | anthropogenic                                   | EDGAR-4.1\(^{a}\) | annual     | 1.04                     |
|              | biomass burning                                 | GFED-2            | monthly    | 0.71                     |
| total        |                                                 |                   |            | 16.17                    |
| OCNN04       | terrestrial biosphere                           | ORCHIDEE OCN      | monthly    | 10.83                    |
|              | ocean                                           | Nevison et al. 2004 | monthly | 4.44                     |
|              | anthropogenic                                   | EDGAR-4.1         | annual     | 1.04                     |
|              | biomass burning                                 | GFED-2            | monthly    | 0.71                     |
| total        |                                                 |                   |            | 17.02                    |
| BWMN04       | natural ecosystem                               | Bouwman et al. 2002 | monthly | 4.59                     |
|              | ocean                                           | Nevison et al. 2004 | monthly | 4.44                     |
|              | anthropogenic and agriculture                    | EDGAR-4.1\(^{b}\) | annual     | 4.54                     |
|              | biomass burning                                 | GFED-2            | monthly    | 0.71                     |
| total        |                                                 |                   |            | 14.28                    |

\(^{a}\) EDGAR categories: 6B, 6A-6C, 3, 1B, 1A3bce, 1A2-2, 1A4-5, 1A3d, 7.

\(^{b}\) EDGAR categories: 6B, 6A-6C, 3, 1B, 1A3bce, 1A2-2, 1A4-5, 1A3d, 7, 4.

and, therefore, not included in the analysis. A 1-year spin-up was considered sufficient as all models started already with their best-estimated initial conditions taken from previous model integrations.

2.2 Prior fluxes

Four different N\(_2\)O emission scenarios were provided to investigate the influence of varying terrestrial and ocean fluxes. All scenarios were comprised of fluxes from the terrestrial biosphere, oceans, biomass burning, waste, fuel combustion and industry and differed only in the estimate of either the terrestrial biosphere or the ocean fluxes (see Tables 2 and 3). Each component flux used to build the scenarios is described below (these were originally provided at monthly temporal and 1.0\(^{\circ}\) \(\times\) 1.0\(^{\circ}\) spatial resolution unless otherwise stated):

1. Terrestrial biosphere: includes fluxes from natural and cultivated ecosystems from the ORCHIDEE O-CN terrestrial biosphere model (Zaehle and Friend, 2010). The model is driven by climate data (CRU-NCEP) and inter-annually varying N inputs. Data were originally provided at 3.75\(^{\circ}\) \(\times\) 2.5\(^{\circ}\) (longitude by latitude) resolution. These fluxes are referred to as OCN.

2. Natural ecosystem: fluxes from uncultivated ecosystems from the empirical model of Bouwman et al. (2002). These fluxes are annual only and are a climatological mean.
Agriculture: fluxes from cultivated ecosystems from EDGAR-4.1 at annual resolution (Emission Database for Greenhouse gas and Atmospheric Research, available at: http://edgar.jrc.ec.europa.eu/index.php). These fluxes together with the natural ecosystem fluxes of Bouwman et al. (2002) are referred to as BWM.

Waste, combustion and industry: fluxes from fossil fuel combustion, industrial solvents, solid and water waste provided by EDGAR-4.1 at annual resolution (data available at: http://edgar.jrc.ec.europa.eu/index.php).

Ocean: three different flux estimates were used. The first estimate, PIC, was taken from the ocean biogeochemistry model, PISCES (Aumont and Bopp, 2006) with an original non-regular resolution of approximately $2^\circ$ longitude $\times 1^\circ$ latitude. The second and third estimates were based on extrapolations of observations of $N_2O$ partial pressure anomalies in the surface ocean that have been coupled to air–sea gas exchange coefficients. The N95 fluxes use the Nevison et al. (1995) estimate at $1.0^\circ \times 1.0^\circ$ resolution, while the N04 fluxes use the Nevison et al. (2004) estimate at $0.5^\circ \times 0.5^\circ$ resolution.

Biomass burning: fluxes from GFED-2.1 (Global Fire Emissions Database; van der Werf et al., 2010). The four flux estimates were then formed using one of the terrestrial biosphere fluxes, OCN or BWM, and one of the ocean fluxes, PIC, N95 or N04, plus the fluxes from biomass burning, waste, combustion and industry. The scenario, OC-NPIC, was used as the control scenario and was used for all model–observation comparisons unless otherwise stated.

Emissions of CFC-12 were provided based on the EDGAR-2 estimate but were scaled to the annual global totals estimated by McCulloch et al. (2003). The global emission in e.g. 2006 was 40 Gg yr$^{-1}$. SF$_6$ emissions were based on the EDGAR-4.1 estimate and were scaled to the top-down global annual totals of Levin et al. (2010). The global emission in 2006 was 6.3 Gg yr$^{-1}$. Both CFC-12 and SF$_6$ emissions were at $1.0^\circ \times 1.0^\circ$ spatial resolution and were linearly interpolated to monthly temporal resolution.

2.3 Transport models

Six models and two of their variants participated in the inter-comparison of modelled $N_2O$ mixing ratios and all of these models have also been included in at least one previous TransCom experiment (Law et al. 2008; Patra et al. 2011). The salient features of each transport model, i.e. the horizontal and vertical resolution and meteorological input, are given in Table 1. All models used meteorological fields from weather forecast models (MERRA, NCEP, JRA25 and ECMWF) either by interpolating (offline models) or by nudging towards fields of horizontal winds and temperature (online models). Model output was generated at each site used in the analysis (see Sect. 2.4): as an hourly average (ACTMt42l32, ACTMt42l67), a 1.5-hourly average (TM5), an interpolation to the observation time step (TM3-NCEP, TM3-ERA) or at the closest model time step to the observation time (in both LMDZ4 and in TOMCAT this is 30 min). Additionally, 3-D fields of monthly mean $N_2O$ mixing ratios were archived (higher temporal resolutions were not considered since this study only looks at seasonal and longer timescales and owing to the large file sizes).

2.4 Observations and data processing

Atmospheric observations of $N_2O$ dry-air mole fractions were pooled from three global networks: NOAA CCGG (National Oceanic and Atmospheric Administration, Carbon Cycle and Greenhouse Gases), NOAA HATS (Halocarbons and other Atmospheric Trace Species) and AGAGE (Advanced Global Atmospheric Gases Experiment), as well as from regular aircraft transects made by NOAA (see Table 4 and Fig. S2). Discrete air samples (flasks) taken in the NOAA CCGG network and in aircraft profiles were analysed for $N_2O$ using GC-ECD (Gas Chromatography with an Electron Capture Detector) and are reported on the NOAA-2006A calibration scale (Hall et al., 2007), and have a reproducibility of 0.4 ppb based on the mean difference of flask pairs. Both NOAA HATS and AGAGE operate networks of in situ GC-ECD instruments. NOAA HATS data are reported on the NOAA-2006A scale (Hall et al., 2007) and have a reproducibility of approximately 0.3 ppb (Thompson et al., 2004) and data from AGAGE are reported on the SIO-1998 scale and have a precision of approximately 0.1 ppb (Prinn et al., 2000). In addition, observations of CFC-12 and SF$_6$ mole
fractions (pmol mol\(^{-1}\), equivalently parts per trillion, ppt) were used from the NOAA HATS and AGAGE networks. Both NOAA HATS measurements were made using in situ GC-ECD while AGAGE measurements of CFC-12 were made using GC-ECD and SF\(_6\) measurements were made with GC Mass Spectrometry (GC-MS). CFC-12 data are reported on the NOAA-2008 (NOAA HATS) and SIO-2005 (AGAGE) scales and SF\(_6\) data are reported on the NOAA-2006 (NOAA HATS) and SIO-2005 (AGAGE) scales.

Surface measurements were filtered for outliers using an iterative filter removing values that were outside two standard deviations of the mean over a time interval of 3 months for flask measurements and 3 days for in situ measurements. Data were available at approximately hourly resolution for in situ data and approximately 2-weekly resolution for flask data. For \(\text{N}_2\text{O}\), calibration offsets between networks, and even between in situ GCs within a network, are considerable compared to the measurement precision; therefore, prior values of these offsets were estimated by comparing time series from different networks and added to the observations for the model–observation comparison (see Table 5).

Mean seasonal cycles were calculated for \(\text{N}_2\text{O}\), CFC-12 and SF\(_6\) by first removing the multi-annual trend, fitted as a second-order polynomial for \(\text{N}_2\text{O}\) and SF\(_6\) and as a third-order polynomial for CFC-12, and then filtering the time series for high-frequency noise using a Butterworth filter. The residuals for each month were then averaged over all years. This method was chosen preferentially over methods involving fitting harmonic curves as these parametrizations impose a strong prior form on the seasonal cycle, which may be unrealistic at sites where the cycle has small amplitude and/or is irregular.

### Results and Discussion

#### 3.1 Large-scale circulation and the influence on \(\text{N}_2\text{O}\)

The atmospheric distribution of \(\text{N}_2\text{O}\) is characterized by a strong cross-tropopause gradient, owing to the loss of \(\text{N}_2\text{O}\) predominantly in the upper stratosphere and STE, and a south-to-north gradient in the troposphere due to stronger emissions in the NH versus the SH. This section examines these large-scale features in the models and assesses them against observational data. In the following discussion, we refer to stratosphere to troposphere transport (STT) as the transport from the stratosphere to the troposphere, which is not to be confused with stratosphere–troposphere exchange (STE), which is a general term for exchange in both directions.

#### 3.1.1 Zonal mean vertical profile

Figure 2 shows the variation of the annual zonal mean \(\text{N}_2\text{O}\) concentration with pressure and latitude for each model using the control flux estimate, OCNPIC (the general features of the zonal mean profiles do not differ from the other flux estimates and are, therefore, not shown). Generally, the large-scale features of the \(\text{N}_2\text{O}\) atmospheric gradient are similar in all simulations. However, they vary in the strength of the tropospheric south-to-north gradient and the gradient across the tropopause and in the stratosphere. The strength of the cross-tropopause gradient is largely determined by the rate of STE, which depends on the strength of the Brewer–Dobson circulation as well as on tropopause folding events, cut-off lows and small-scale mixing associated with upper-level fronts and cyclones (Holton et al., 1995). The Brewer–Dobson circulation oscillates seasonally with air ascending diabatically across the tropopause in the tropics, stratospheric poleward...
transport in the winter hemisphere, and diabatically descending air across the tropopause in the high latitudes in winter (Holton et al., 1995). The seasonal influence of the Brewer–Dobson circulation on \( \text{N}_2\text{O} \) mixing ratios is better resolved in MOZART4, ACTMt42l67, TM5, TM3-ERA and TOMCAT than in the models with low vertical resolution (LMDZ4 with only 19-eta layers) and those with few stratospheric layers (ACTMt42l32 and TM3-NCEP) (see Fig. S1).

The stratosphere can be classified into an “overworld” and an “underworld” to better describe STE. The overworld lies entirely above the 380 K isentrope, while the underworld has the tropopause as its lower bound and the 380 K isentrope as its upper bound. Isentropic surfaces intersect the tropopause in the extra-tropics, lying partly in the lower extra-tropical stratosphere and partly in the troposphere. Air masses can thus be mixed adiabatically between the troposphere and lower stratosphere along isentropes that intersect the tropopause (Holton et al., 1995). Since on annual timescales there is no net change in the mass of the lower stratosphere, exchange across the 380 K isentropic surface can be considered as representative of the net STE (Schoeberl, 2004). This is a particularly useful simplification when considering the budgets of species such as \( \text{N}_2\text{O} \) and CFC-12, which have a source in the troposphere and sink in the stratosphere. Table 6 shows the height of the tropopause and the gradients across the tropopause and the 380 K isentropic

### Table 4. Atmospheric sites used in the analysis.

| ID | Station                  | Network | Type | Latitude (°) | Longitude (°) | Altitude (m a.s.l.) |
|---|-------------------------|---------|------|--------------|---------------|--------------------|
| ALT | Alert                   | NOAA    | F    | 82.5° N      | 62.5° W       | 210                |
| ZEP | Ny-Ålesund              | NOAA    | F    | 78.9° N      | 11.88° E      | 475                |
| BRW | Barrow                  | NOAA    | F, C*| 71.3° N      | 156.6° W      | 11                 |
| MHD | Macehead                | AGAGE   | C, C*| 53.3° N      | 9.9° W        | 25                 |
| SHM | Shemya Island            | NOAA    | F    | 52.7° N      | 174.1° E      | 40                 |
| THD | Trinidad Head           | AGAGE   | C, C*| 41.1° N      | 124.2° W      | 107                |
| NWR | Niwot Ridge             | NOAA    | F, C*| 40.0° N      | 105.5° W      | 3526               |
| IZO | Tenerife                | NOAA    | F    | 28.3° N      | 16.5° W       | 2360               |
| KUM | Cape Kumukahi           | NOAA    | F    | 19.5° N      | 154.8° W      | 3                  |
| MLO | Mauna Loa               | NOAA    | F, C*| 19.5° N      | 155.6° W      | 3397               |
| RPB | Ragged Point            | AGAGE   | C, C*| 13.2° N      | 59.4° W       | 45                 |
| CHR | Christmas Island        | NOAA    | F    | 1.7° N       | 157.2° W      | 3                  |
| SEY | Seychelles              | NOAA    | F    | 4.7° S       | 55.2° E       | 3                  |
| ASC | Ascension Island        | NOAA    | F    | 7.9° S       | 14.4° W       | 54                 |
| SMO | Samoa                   | AGAGE   | C, C*| 14.3° S      | 170.6° W      | 42                 |
| EIC | Easter Island           | NOAA    | F    | 27.2° S      | 109.5° W      | 50                 |
| CGO | Cape Grim               | AGAGE   | C, C*| 40.7° S      | 144.7° E      | 164                |
| TDF | Tierra del Fuego        | NOAA    | F    | 54.9° S      | 68.5° W       | 20                 |
| HBA | Halley Station          | NOAA    | F    | 75.6° S      | 26.5° W       | 30                 |
| SPO | South Pole              | NOAA    | F, C*| 89.98° S     | 24.8° W       | 2810               |

F = flask measurement.  
C = continuous (in situ) measurement.  
C* = continuous (in situ) measurement of CFC-12 and SF6.  
A = aircraft flask measurement.  
** Metres above sea level.

### Table 5. Calibration offsets relative to the NOAA2006A scale.

| Site          | Mean offset (ppb) |
|---------------|-------------------|
| MHD           | 0.25              |
| THD           | –0.30             |
| RPB           | 0.00              |
| SMO           | 0.20              |
| CGO           | 0.20              |

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Table 6. Annual mean height of the tropopause (hPa) and the N\textsubscript{2}O gradient (ppb) across the tropopause (cross-tropopause CT) and the 380 K isentrope. Tropics are defined as between 10\textdegree\ S and 10\textdegree\ N and extra-tropics are defined as latitudes higher than 30\textdegree\.

| Model       | Tropopause height | CT gradient\textsuperscript{a} | Gradient across 380 K\textsuperscript{b} |
|-------------|-------------------|-------------------------------|----------------------------------|
|             | Tropics           | Extra-tropics                 | Tropics                          | Extra-tropics |
| MOZART4     | 103               | 239                           | 1.0                              | 0.6           | 1.0                          | 4.2                          |
| ACTM\textsuperscript{4}2132 | 105               | 232                           | 0.2                              | 1.0           | 0.2                          | 3.1                          |
| ACTM\textsuperscript{4}2167 | 106               | 233                           | 0.1                              | 0.9           | 0.1                          | 3.3                          |
| TM5         | 105               | 233                           | 2.6                              | 1.3           | 2.6                          | 5.5                          |
| TM3-NCEP    | 101               | 234                           | 0.5                              | 0.3           | 0.5                          | 1.5                          |
| TM3-ERA     | 105               | 236                           | 0.6                              | 0.4           | 0.6                          | 2.6                          |
| LMDZ4       | 109               | 226                           | 6.2                              | 0.3           | 6.2                          | 8.0                          |
| TOMCAT      | 102               | 238                           | 0.6                              | 1.3           | 0.6                          | 3.3                          |

\textsuperscript{a} Normalized to a CT pressure difference of 10hPa.
\textsuperscript{b} Normalized to a pressure difference across the 380 K isentrope of 10hPa.

Fig. 3. Modelled and observed N\textsubscript{2}O growth rates (ppb/y) versus lifetimes (y). Legend: Mozart4, yellow; ACTM\textsuperscript{4}2132, blue; ACTM\textsuperscript{4}2167, green; TM5, grey-blue; TM3-NCEP, purple; TM3-ERA, red; LMDZ4, magenta; TOMCAT, dark green; observed (covering the range of estimated lifetimes), black line.

3.1.2 Growth rate and lifetime

The tropospheric growth rate of N\textsubscript{2}O is determined by the sum of the surface emissions and the net flux of N\textsubscript{2}O across the tropopause and, on annual timescales, across the 380 K isentrope. Since all models use the same prior fluxes (OC-NPIC), differences in the modelled growth rates are due directly to differences in the net cross-tropopause N\textsubscript{2}O flux, which depend on the upward and downward mass fluxes and on the above- and below-tropopause N\textsubscript{2}O mixing ratios, factors that are determined by the meteorological data used as well as on the vertical definition of the models. Table 7 shows the annual mean (2006–2009) tropospheric N\textsubscript{2}O growth rates, total abundance, total sink and the atmospheric lifetime of N\textsubscript{2}O. Tropospheric growth rates were calculated in both the models and the observations as the mean growth rate at background surface sites (these were ZEP, BRW, ALT, SHM, MHD, THD, IZO, KUM, MLO, RPB, CHR, SEY, SMO, ASC, EIC, CGO, TDF, HBA and SPO; for a description of the sites see Table 4). The total sink was calculated directly by adding up the loss at each time step (except in ACTM\textsuperscript{4}2132 where it was calculated as the difference between the total source and the change in total burden) and the lifetime was calculated as the atmospheric N\textsubscript{2}O abundance up to approximately 50 hPa divided by the global annual loss. Most models have tropospheric growth rates close to the observed rate of 0.84 ppb yr\textsuperscript{-1} with the exceptions of ACTM\textsuperscript{4}2132 and LMDZ4, which have substantially lower rates. Figure 3 shows the relationship between growth rate and lifetime for the observations and models. Although in ACTM\textsuperscript{4}2132 the low growth rate can be explained by the anomalously large sink (16 TgN yr\textsuperscript{-1}) and correspondingly short lifetime (92 years), in LMDZ4 it is not so straightforward. LMDZ4 has been shown to be a relatively diffuse model with fast venting of the planetary boundary layer (PBL) (Geels et al., 2007), which results in N\textsubscript{2}O being mixed too rapidly into higher altitudes and insufficient accumulation of N\textsubscript{2}O in the PBL. TOMCAT, despite capturing the growth rate, has a shorter lifetime owing to the low abundance of N\textsubscript{2}O in the troposphere and stratosphere. The problems in LMDZ4 and TOMCAT could be rectified at least...
Table 7. Annual mean (2006–2009) tropospheric growth rate, atmospheric lifetime, atmospheric abundance (up to 50 hPa) and global total sink of N\textsubscript{2}O.

| Growth rate (ppb yr\textsuperscript{−1}) | Lifetime (years) | Abundance (TgN) | Sink (TgN yr\textsuperscript{−1}) |
|-----------------------------------------|-----------------|----------------|-----------------
| Observed                                | 0.84            | 124–130\textsuperscript{*} | –   | –   |
| MOZART4                                | 0.99            | 128            | 1608          | 12.6 |
| ACTM\textsubscript{4}2l32               | 0.52            | 92             | 1489          | 16.2 |
| ACTM\textsubscript{4}2l67               | 0.84            | 119            | 1470          | 12.4 |
| TM5                                     | 0.76            | 125            | 1544          | 12.4 |
| TM3-NCEP                                | 0.76            | 121            | 1515          | 12.5 |
| TM3-ERA                                 | 0.86            | 126            | 1571          | 12.5 |
| LMDZ4                                   | 0.24            | 119            | 1496          | 12.6 |
| TOMCAT                                  | 0.86            | 108            | 1352          | 12.5 |

\textsuperscript{*} Independent estimates of the lifetime (Prather et al., 2012; Volk et al., 1997).

Table 8. Correlations of modelled and observed zonal mean meridional gradients for different flux scenarios (mean 2006–2009). Also shown are the inter-hemispheric differences (IHD) calculated as the mean of values for all background sites north of 20\degree N minus the mean of all values for sites south of 20\degree S. The observed IHD for N\textsubscript{2}O and SF\textsubscript{6} were 1.44 ppb and 0.36 ppt, respectively. R values in brackets were not significant at the 95\% confidence level.

| Model       | OCNPIC | OCNN04 | OCNN95 | BWMM04 | SF\textsubscript{6} |
|-------------|--------|--------|--------|--------|---------------------|
|             | R      | IHD    | R      | IHD    | R                   | IHD    | R      | IHD    | R      | IHD    |
| MOZART4     | 0.90   | 0.60   | –      | –      | –                   | –      | –      | –      | –      | –      |
| ACTM\textsubscript{4}2l32 | 0.89   | 1.00   | 0.88   | 1.01   | 0.85                | 1.09   | 0.85   | 0.96   | –      | –      |
| ACTM\textsubscript{4}2l67 | 0.94   | 1.11   | 0.91   | 1.09   | 0.89                | 1.16   | 0.89   | 0.97   | 0.90   | 0.41   |
| TM5         | 0.95   | 1.06   | 0.93   | 1.09   | 0.89                | 1.16   | 0.88   | 0.93   | –      | –      |
| TM3-NCEP    | –0.04  | –0.18  | –0.26  | –0.27  | –0.27               | –0.20  | –0.42  | –0.31  | –      | –      |
| TM3-ERA     | 0.91   | 0.72   | 0.85   | 0.72   | 0.81                | 0.79   | 0.79   | 0.56   | 0.99   | 0.39   |
| LMDZ4       | 0.58   | 0.16   | 0.42   | 0.11   | 0.46                | 0.17   | 0.02   | –0.01  | 0.91   | 0.69   |
| TOMCAT      | 0.78   | 0.98   | 0.83   | 0.96   | 0.84                | 0.97   | 0.86   | 0.76   | 0.87   | 0.50   |

to some extent by using longer spin-up times, which would bring the vertical gradients closer to steady state.

3.2 Tropospheric transport

3.2.1 Vertical gradients

Vertical mixing ratio gradients represent the combined influence of surface fluxes and atmospheric transport. For N\textsubscript{2}O, the surface fluxes are largely from the land and these are predominantly positive, therefore the mixing ratio generally decreases with altitude. Sites located in the interior or downwind of continents show stronger gradients than those downwind of ocean basins owing to the stronger influence of land fluxes. However, at sites where there are only weak surface fluxes, the gradient may be heavily influenced by lateral transport and in some cases become positive in the troposphere. Figure 4 shows the seasonal and annual mean modelled (using the OCNPIC flux scenario) and observed vertical gradients of N\textsubscript{2}O mixing ratio at the NOAA GMD aircraft profiling sites: Raratonga (RTA, 21\degree S, 160\degree E), Hawai\textsuperscript{i} (HAA, 21\degree N, 158\degree W), Ulaanbaatar (ULB, 47\degree N, 106\degree E) and Poker Flats (PFA, 65\degree N, 147\degree W). For all vertical gradients (from the surface to 6000 m), the mean modelled/observed tropospheric mixing ratio at each station has been subtracted. At RTA, located in the South Pacific, a strong positive N\textsubscript{2}O gradient of approximately 0.8 ppb (0 to 6000 m) is observed in June–August, as well as in the annual mean, while no significant gradient is observed in December–February. A similar feature is also seen in the SF\textsubscript{6} profiles at this site (not shown). The seasonal change in gradient corresponds with the north–south oscillation of the inter-tropical convergence zone (ITCZ). In the NH summer the ITCZ lies north of the Equator, thus air from the NH tropics, which has a higher N\textsubscript{2}O mixing ratio, is mixed into the southern Hadley cell and descends in the SH sub-tropics. Only the two CTM models and TOMCAT approximately capture the strength of the gradient but in TOMCAT, the maximum mixing ratio occurs at too low altitude. The other models (MOZART4, TM5, TM3-NCEP, TM3-ERA and LMDZ4) all underestimate the June–August and annual mean gradients to varying degrees. This appears not to be simply related to the inter-hemispheric (IH) exchange time, as TM5 has a long IH
exchange time, while in LMDZ4 it is relatively short and in MOZART4 it is close to that observed (Patra et al., 2011). At HAA, located in the North Pacific, the air column above the PBL is very well mixed owing to the absence of strong local sources and to vigorous vertical mixing. All models are able to reproduce the observed vertical profile at this site. ULB is a mid-latitude station in central Mongolia. A negative vertical gradient is observed in all seasons, except autumn when it is positive, and has an annual mean value of approximately 0.4 ppb (from 1500 to 4000 m). The gradient is underestimated by all models (with the exception of TOMCAT in June–August) suggesting that either the emissions are underestimated in central Asia or that the modelled vertical mixing for this region is too strong. Although we cannot rule out the first possibility, the latter is consistent with previous studies, which found a systematic overestimate of vertical mixing in the troposphere in northern mid-latitudes by CTMs (e.g. Stephens et al., 2007). At the high northern latitude site, PFA in Alaska, weak negative gradients are observed, approximately 0.2 ppb (1000 to 6000 m) for the annual mean. The gradient becomes stronger in December–February above 5000 m owing to the descent of N\textsubscript{2}O-poor air from the lower stratosphere. At this site, the shape and strength of the gradient is fairly well reproduced by all models, a feature which is discussed further in Sect. 3.3.1 in relation to the N\textsubscript{2}O seasonal cycle in the high northern latitudes.

### 3.2.2 Meridional gradients

Meridional gradients and IH differences are some of the most commonly used constraints on tropospheric transport (Gloor et al., 2007; Patra et al., 2011). Patra et al. (2011) showed that most state-of-the-art transport models agree closely in the IH gradient of SF\textsubscript{6} (for which the emissions are fairly well known) as well as in the IH exchange rate. This study similarly finds good agreement with the observed SF\textsubscript{6} IH difference for all models that provided SF\textsubscript{6} simulations; however, the agreement is much poorer for N\textsubscript{2}O (Figs. 5 and 6). Here the IH difference is calculated as the difference between the mean of all mixing ratios at background sites between 20–90° S and 20–90° N. All transport models underestimate the N\textsubscript{2}O IH difference, regardless of which prior flux scenario is used (Table 8 and Fig. S3). The scenario BWMN04 results in the lowest IH differences for all models, while differences among the “OCN” scenarios are small and not consistent for all models. Considering the good agreement, or in some cases even overestimate, for SF\textsubscript{6}, the poor agreement in the IH difference for N\textsubscript{2}O is likely due to an inaccurate distribution of emissions between the NH and SH and/or too strong STT in the NH relative to the SH. The ocean N\textsubscript{2}O flux estimates from Nevison et al. (1995, 2004) have been shown to overestimate the net ocean–atmosphere flux in the Southern Ocean (Hirsch et al., 2006; Huang et al., 2008) but this overestimate alone is not sufficient to explain the model–observation mismatch in the IH difference. Approximately, a difference of 6.5 TgN between the NH and SH emissions is needed to explain the observed IH mixing ratio difference of 1.44 ppb. With all models underestimating the observed gradient by at least 0.33 ppb (23 %), which is equivalent to a mass of approximately 1.5 TgN, assuming the overesti-
mate of the Southern Ocean emissions to be approximately 1.0 TgN (Hirsch et al., 2006) leaves an unexplained north–south difference of 0.5 TgN. This could be due to errors in STT in the NH or it could be that there is still a bias in NH versus SH emissions, which could be corrected by a combination of reducing SH emissions and increasing NH emissions. The distribution of emissions within each hemisphere also influences how well each model captures the meridional gradient. The interplay between emissions and transport errors in each model explains why the models do not all respond in the same way to the different flux scenarios, with respect to the IH difference and meridional gradient.

3.3 Factors determining the seasonality of N₂O

The seasonality of N₂O is determined by a combination of STT, tropospheric transport and surface fluxes (Ishijima et al., 2010). However, the importance of each of these determinants, and how this changes with latitude, remains uncertain.
Nevison et al. (2007, 2011) have demonstrated the importance of seasonality in STT for the N$_2$O seasonal cycle in the troposphere but this mechanism appears to be less important in mid-to-low latitudes where seasonality in the surface fluxes are significant (Ishijima et al., 2010). We examine the varying influences on the tropospheric N$_2$O seasonal cycle focusing on seven sites, which cover a wide range of latitudes: BRW, MHD, THD, MLO, SMO, CGO and SPO (see Table 4). While most are background sites, MHD, CGO and THD are affected by local- to regional-scale fluxes. MHD is periodically influenced by transport from the European continent (Biraud et al., 2002; Manning et al., 2011) and CGO is occasionally influenced by transport from southeastern Australia (Wilson et al., 1997). THD is affected by transport from the North American continent and, in the case of N$_2$O, by N$_2$O emissions from upwelling along the Californian coast (Lueker et al., 2003). THD is also a difficult site to model owing to the strong land/sea breeze cycle. Although this is not reproduced in global models, we expect the error in the simulated N$_2$O due to transport to be considerably smaller than for CO$_2$ since there is no significant diurnal cycle in N$_2$O fluxes, thus there is no diurnal rectifying effect.

Only ACTM+4267, TM3-ERA, LMDZ4 and TOMCAT participated in the CFC-12 and SF$_6$ inter-comparisons, thus we have results for all three species from only these four models. The results of the inter-comparisons are presented in the following sections.

3.3.1 Influence of STT and tropospheric transport

To examine the influence of STT on the tropospheric seasonal cycle, we compare with CFC-12 because, like N$_2$O, the CFC-12 seasonal cycle is strongly influenced by STT (Liang et al., 2009; Nevison et al., 2007) but, unlike N$_2$O, the seasonality in the surface fluxes is likely to be only very small. The phase of the modelled seasonal cycle, i.e. the month of the minimum, for CFC-12 (upper panel) and N$_2$O (lower panel) is shown as a function of latitude and pressure in Fig. 7. In all models, the NH CFC-12 and N$_2$O minima appear in the lower stratosphere and upper troposphere in winter and reach the lower troposphere in May–June in the low to mid latitudes and in July–August in the high latitudes (TM3-NCEP is an exception as the minima occur about 1 month earlier compared to the other models). In the SH, the modelled minima appear in the lower stratosphere and upper troposphere in the austral spring to early summer, following the breakup of the polar vortex (except in TM3-NCEP where this is circa 2 months later). There is a lag of circa 1 to 3 months for the minima to reach the lower troposphere, where this occurs between January and April. We first examine the modelled seasonality in the lower troposphere by comparing with observations of N$_2$O, CFC-12 and SF$_6$ from the AGAGE and NOAA surface networks, and second, examine the N$_2$O seasonality at altitude by comparing with observations from NOAA flight profiles. Figure 8 shows the mean seasonal cycle (2006–2009) in N$_2$O, CFC-12 and SF$_6$ at AGAGE and NOAA surface sites. The seasonal cycle amplitudes have been normalized by the mean tropospheric abundance of each species to simplify the comparison between them.

Northern Hemisphere

In the mid-to-high northern latitudes, a minimum in N$_2$O and CFC-12 is observed on average in August but for N$_2$O the timing varies from July to September depending on the year. At BRW and MHD, a considerable phase shift in the modelled N$_2$O seasonal cycle can be seen with respect to the observations, with the modelled minimum occurring between 2 and 4 months too early (Fig. 8). For CFC-12, however, the modelled seasonality coincides with the observations at MHD and is only circa 1 month too early at BRW (one exception is TM3-ERA at MHD, which has no clear seasonal cycle). The good agreement for CFC-12 for most models indicates that transport of air from the lower stratosphere into the troposphere in the high northern latitudes is adequately represented and, therefore, suggests that the model–observation phase shift in N$_2$O at these two sites is at least in part due to incorrect seasonality in emissions in the northern mid-to-high latitudes (this will be discussed further in Sect. 3.3.2). At THD the observed and modelled seasonality in CFC-12 closely resembles that at MHD and BRW, whereas for N$_2$O the seasonality observed at THD has only circa half the amplitude and the phase is quite different with respect to MHD and BRW. This points to a significant influence of N$_2$O surface fluxes on the observed seasonal cycle at this site, as also found by Nevison et al. (2011), and is most likely out of phase with the STT influence (also discussed further in Sect. 3.3.2). In the tropics, at MLO, the observed seasonality in N$_2$O and CFC-12 has the same phase but only about a quarter of the amplitude of that seen at BRW while the modelled N$_2$O cycle, in contrast, has approximately the same amplitude as at BRW. The overestimate in the amplitude of the modelled seasonal cycle at MLO is most likely due to an overestimate of the influence of STT at this site (as indicated by the timing of the minimum, i.e. in May, consistent with the modelled maximum in STT and a 3-month lag from the tropopause to the lower troposphere) and to the problem in the seasonality of emissions in the northern mid-to-high latitudes (see Sect. 3.3.2).

From the comparison of the observed seasonal cycles in the NH, a small shift to later CFC-12 and N$_2$O minima with increasing latitude was found (see Table 9) (THD is an exception as the N$_2$O seasonal cycle is strongly influenced by local land and ocean fluxes). The shift to later minimum with increasing latitude is also reproduced by most of the models (Fig. 7) and is consistent with the current understanding of STT. Air masses from the lower stratosphere are more strongly mixed into the troposphere in the extra-tropics.
Table 9. Day of the year for the occurrence of the minimum in the mean seasonal cycle (2006–2009) of N\textsubscript{2}O, CFC-12 and SF\textsubscript{6} at each of the background sites.

| Model         | Species | BRW  | MHD | THD  | MLO  | SMO  | CGO  | SPO  |
|---------------|---------|------|-----|------|------|------|------|------|
| Observed N\textsubscript{2}O | 242     | 238  | 276 | 229  | 228  | 135  | 127  |
| Observed CFC-12 | 232     | 232  | 217 | 201  | 217  | 113  | 139  |
| Observed SF\textsubscript{6}   | 266     | 254  | 248 | 215  | 246  | 39   | 50   |
| MOZART4 N\textsubscript{2}O | 162     | 136  | 78  | 138  | 142  | 122  | 44   |
| MOZART4 CFC-12 | –       | –    | –   | –    | –    | –    | –    |
| MOZART4 SF\textsubscript{6}   | –       | –    | –   | –    | –    | –    | –    |
| ACTMt42l32 N\textsubscript{2}O | 189     | 181  | 169 | 141  | 235  | 123  | 185  |
| ACTMt42l32 CFC-12 | –       | –    | –   | –    | –    | –    | –    |
| ACTMt42l32 SF\textsubscript{6} | –       | –    | –   | –    | –    | –    | –    |
| ACTMt42l67 N\textsubscript{2}O | 187     | 176  | 171 | 145  | 228  | 117  | 115  |
| ACTMt42l67 CFC-12 | 223     | 233  | 211 | 143  | 270  | 90   | 95   |
| ACTMt42l67 SF\textsubscript{6} | 242     | 241  | 219 | 43   | 186  | 40   | 55   |
| TM5 N\textsubscript{2}O | 171     | 164  | 154 | 154  | 273  | 85   | 93   |
| TM5 CFC-12 | –       | –    | –   | –    | –    | –    | –    |
| TM5 SF\textsubscript{6}   | –       | –    | –   | –    | –    | –    | –    |
| TM3–NCEP N\textsubscript{2}O | 136     | 123  | 122 | 125  | 243  | 253  | 173  |
| TM3–NCEP CFC-12 | –       | –    | –   | –    | –    | –    | –    |
| TM3–NCEP SF\textsubscript{6} | –       | –    | –   | –    | –    | –    | –    |
| TM3-ERA N\textsubscript{2}O | 169     | 152  | 156 | 150  | 250  | 59   | 75   |
| TM3-ERA CFC-12 | 206     | 233  | 190 | 142  | 249  | 44   | 54   |
| TM3-ERA SF\textsubscript{6} | 225     | 57   | 210 | 54   | 190  | 48   | 51   |
| LMDZ4 N\textsubscript{2}O | 201     | 184  | 173 | 143  | 277  | 294  | 319  |
| LMDZ4 CFC-12 | 183     | 316  | 170 | 182  | 41   | 149  | 60   |
| LMDZ4 SF\textsubscript{6} | 211     | 239  | 189 | 231  | 276  | 41   | 38   |
| TOMCAT N\textsubscript{2}O | 167     | 131  | 133 | 178  | 323  | 127  | 97   |
| TOMCAT CFC-12 | 235     | 227  | 222 | 219  | 330  | 110  | 97   |
| TOMCAT SF\textsubscript{6} | 255     | 262  | 22  | 18   | 344  | 19   | 44   |

Southern Hemisphere

In SH high latitudes, the observed N\textsubscript{2}O and CFC-12 seasonal cycles differ significantly to those of the NH (i.e. they are not 6 months out of phase). Most models predict the minimum at SPO in January–February, i.e. too early by circa 2 months (ACTMt42l32 is an exception where the N\textsubscript{2}O minimum is about 2 months too late). However, for SF\textsubscript{6}, the models match the observed cycle reasonably well at CGO and SPO. This can be understood in that the SF\textsubscript{6} seasonal cycle in the SH is largely due to seasonality in IH exchange and the strong meridional gradient in the atmosphere (Denning et al., 1999; Prinn et al., 2000), which is satisfactorily represented in the models. On the other hand, the N\textsubscript{2}O and CFC-12 seasonal cycles are strongly modulated by STT and, in the case of N\textsubscript{2}O, weakly modulated by ocean fluxes. The importance of STT has been shown previously at CGO using measurements of CFC-11 and CFC-12 (Nevison et al. 2005) and \delta\textsubscript{18}O and \delta\textsubscript{15}N isotopes in N\textsubscript{2}O (Park et al., 2012). The model–observation mismatch for N\textsubscript{2}O and CFC-12 points to a deficiency in modelling STT in the SH. However, it is not easy to explain why the maximum influence of STT (resulting in a minimum in N\textsubscript{2}O and CFC-12) is seen in April–May, which is 2 to 3 months later than one would expect given the winter (May to August) maximum in diabatic STT, the spring increase in tropopause height, and the spring breakup of the polar vortex, and points to gaps in our knowledge about STT in the SH. The observed seasonal cycles of N\textsubscript{2}O and CFC-12 at SMO are closely in phase with that of SF\textsubscript{6}, which can be explained in terms of IH transport and the north–south

where the transport can occur adiabatically along isentropes intersecting the tropopause (James et al., 2003; Stohl et al., 2003). Furthermore, once air masses cross the tropopause, they can be rapidly transported to the lower troposphere in the downward branch of the Hadley cell around 30\textdegree N (James et al., 2003). Therefore, the minimum is observed earlier in the mid-latitudes than in the high latitudes where the rate of vertical transport is slower. Stratospheric air masses are then transported with the mean tropospheric meridional circulation towards higher latitudes. Considering this, the small phase shift in modelled CFC-12 (and part of the N\textsubscript{2}O phase shift) compared with the observations at BRW may in fact be due to too rapid transport within the troposphere rather than too rapid or too early mixing across the tropopause.
mixing ratio gradient and is consistent with previous studies (Nevison et al., 2007).

Altitude changes

To further investigate the influence of STT, we compare the modelled seasonal cycles at four different altitude ranges, from the lower troposphere to the tropopause, with NOAA aircraft data (unfortunately there is insufficient data coverage at RTA to be able to compare the seasonal cycles at this site). Figure 9 shows the observed and modelled $\text{N}_2\text{O}$ as monthly means with the growth rate subtracted (as given in Table 7). At PFA, the influence of STT is seen between 6000 and 10,000 m with an observed minimum occurring...
in late June. The timing of this minimum appears to be inconsistent with a winter maximum in diabatic STT due to the Brewer–Dobson circulation. However, as pointed out by Schoeberl (2004), most of the mass exchange between the lower stratosphere and troposphere can be related to changes in the tropopause height with the maximum mass transfer to the troposphere occurring in spring as the tropopause height is increasing – in which case, allowing for the lag time for vertical and horizontal transport within the troposphere of approximately 2 months according to Liang et al. (2009), a June minimum is not unexpected. Another consideration for the timing of the minimum is the seasonal cycle of \(N_2O\) in the stratosphere itself, which must be convolved with that of STT to explain the influence on tropospheric seasonality (Liang et al., 2009). Since \(N_2O\) is destroyed photochemically, extratropical stratospheric loss of \(N_2O\) has a maximum in summer and minimum in winter, thus the phase of the seasonal cycle in the stratosphere will lead to a later minimum in the troposphere (as compared to no seasonality in the stratosphere). Below 6000 m, the minimum occurs significantly later again, in August. The reason for the August minimum is likely twofold: (1) owing to the time needed to transport the STT influence in the mid-latitudes (where most STT occurs) to the high northern latitudes and (2) owing to the increase in PBL height, which means the fluxes are mixed into a greater volume of air, thereby decreasing the mixing ratio. Although all models predict a too early minimum above 6000 m (by circa 2.5 months), the phase shift between the modelled and observed minima is fairly constant across all altitudes, consistent with the finding that the modelled vertical gradient at this site agrees with observations (see Fig. 4).

At ULB, the influence of STT can be seen between 4000 and 6000 m with a minimum in July but the amplitude of the cycle decreases at lower altitudes suggesting a weaker influence of STT in the lower troposphere at this latitude. Although the phase of the cycle in the 4000–6000 m altitude range is fairly closely captured by most models, they overestimate its amplitude below 4000 m. Lastly, at HAA, the observed seasonal cycle is consistent in amplitude and phase from 500 to 6000 m, owing to vigorous vertical mixing. However, all models predict a too early minimum below 6000 m and overestimate the amplitude suggesting that the modelled influence of STT at this latitude is too strong.

### 3.3.2 Influence of surface fluxes

The influence of changing the surface fluxes of \(N_2O\) on the seasonal cycle in the lower troposphere was investigated by performing four different transport model integrations with each of the four prior flux estimates: OCNPIC, OCNN95, OCNN04 and BWMN04 (see Tables 2 and 3 for details and
Fig. 10. Comparison of observed mean $N_2O$ seasonality (2006–2009) with that modelled using four different prior flux models. Each station is shown as a separate panel and within each panel the four subplots are for each of the flux models as indicated in the top-left corner (see Tables 2 and 3 for a description of the fluxes). $N_2O$ mixing ratio is on the left axis and $N_2O$ flux (grey line) is on the right axis. Legend: Mozart4, yellow; ACTMt42I32, blue; ACTMt42I67, green; TM5, grey-blue; TM3-NCEP, purple; TM3-ERA, red; LMDZ4, magenta; TOMCAT, dark green; observed, black.

Fig. S4 for Hovmöller plots of the flux components. Figure 10 compares the observed and modelled seasonal cycles at each site (BRW, MHD, THD, MLO, SMO and CGO) as a separate panel, and the four subplots within each panel are for each of the four flux scenarios. Also shown within each subplot is the area-weighted mean $N_2O$ flux for an area of $10° \times 30°$ (latitude by longitude) centred on the site. At BRW, the best match to the observed cycle was provided by the BWMN04 fluxes while the other three (all using OCN terrestrial biosphere fluxes) were very similar in phase and amplitude. Around the site itself, the flux is very low and there is little difference between the BWM and OCN terrestrial fluxes (the flux difference is solely due to the choice of ocean flux estimate). The improved fit to the seasonal cycle
in the mixing ratio at BRW, therefore, must result from the
difference between OCN and BWM in the mid-northern latitudes;
OCN predicts a late summer maximum while there is no seasonal cycle in BWM. The phase modelled with
BWMN04 matches almost exactly (correlation coefficient
$R^2 \geq 0.95$) for all models except TM3-NCEP. Furthermore,
considering that for CFC-12 at this site there is a phase shift
of only approximately 1 month, the mismatch in the OCN
simulations is unlikely to be from transport model errors.
Similarly at MHD, BWMN04 provides the best fit to the
observations ($R^2 \geq 0.79$, except TM3-NCEP). These results
show that the inclusion of a seasonal cycle in the OCN ter-
restrial fluxes does not improve the fit to the observations but
rather makes it worse, indicating that the seasonality, in par-
special the late summer maximum, in OCN is not realistic.
From what is known about the processes driving the terres-
trial biosphere N$_2$O flux, higher emissions are expected dur-
during the growing season owing to warmer soil temperatures
leading to increased microbial activity and higher reactive
nitrogen turnover rates. However, OCN most likely overesti-
mates the late summer emissions while underestimating
the emissions in spring and early summer. This is due to the
lack of a vertically resolved soil layer, which prevents the
realistic simulation of the impact of rain events and tends to
predict anoxic soil conditions, necessary for N$_2$O pro-
duction via denitrification, predominantly in summer rather
than distributed throughout the year as would be more real-
istic (S. Zaehle, personal communication, 2012). This result
highlights the complexity of modelling terrestrial ecosystem
N$_2$O fluxes and the need for independent validation. Again at
THD, BWMN04 gives the closest fit to the observed seasonal
cycle matching the amplitude but still resulting in a too early
minimum by circa 3 months. Since THD is also strongly in-
fluenced by N$_2$O emissions from upwelling along the Cali-
ifornian coast (Lueker et al., 2003), this model–observation
mismatch may also indicate deficiencies in the coastal N$_2$O
fluxes.

At MLO, the regional flux differences are due to differ-
cences between the ocean flux models, PIC, N95 and N04.
However, an improvement in the modelled seasonal cycle
in N$_2$O mixing ratio only occurs when the BWM terrestrial
fluxes are used ($R^2 \geq 0.27$, except TM3-NCEP, compared
with no correlation with the other fluxes). This shows that
the seasonality at MLO is also influenced by NH terrestrial
fluxes as has also been previously shown (Patra et al., 2005).
For SMO, the modelled seasonality is very similar for all flux
models (N04 results in a small phase shift to a later mini-
mum), which can be understood in that this site is strongly
affected by IH exchange rather than the seasonality of sur-
face fluxes in this latitude. In the southern mid-latitudes, at
CGO, OCN and OCN95 give the best agreement to the
observed seasonal cycle. Replacing the terrestrial biosphere
fluxes, OCN, with BWM made no significant difference, as
expected since this site is only very weakly influenced by
land fluxes. For SPO, changing the fluxes had negligible in-
fluence on the modelled mixing ratios (this site is not shown),
highlighting again the importance of STT at this site.

4 Summary and conclusions

This TransCom study has investigated the influence of emis-
sions, tropospheric transport and stratosphere–troposphere ex-
change (STE) on the variability in atmospheric N$_2$O, fo-
cusing on seasonal to annual timescales. In particular, our
aim has been to examine the influence of errors in atmos-
pheric transport versus errors in prior fluxes on modelled
mixing ratios by comparing simulated mixing ratios with at-
mospheric observations of N$_2$O as well as CFC-12 to as-
ssess the ability of models to reproduce STE and, addition-
ally, of SF$_6$ to assess the tropospheric transport in the models.
Knowledge about prior flux and transport errors has impor-
tant implications for the setup of inverse models for estimat-
ing N$_2$O surface emissions and for the interpretation of their
results. In total, six different transport models and two model
variants were included in this inter-comparison.

To assess the representation of global-scale transport and,
in particular, inter-hemispheric transport, we compared the
modelled and observed IH gradients of N$_2$O and SF$_6$. We
found good agreement between the modelled and observed
south-to-north gradient and IH difference for SF$_6$ in line with
previous studies (e.g. Patra et al., 2011), which indicates that
the models adequately capture the rate of IH mixing as well
as mixing between tropical and extra-tropical regions. For
N$_2$O, however, the IH difference was underestimated com-
pared to the observations in all models by at least 0.33 ppb,
equivalent to approximately 1.5 TgN. Assuming that emis-
sions in the Southern Ocean are overestimated by approxi-
imately 1.0 TgN (Hirsch et al., 2006) leaves an unexplained
large NH to SH source ratio than prescribed in the prior
emissions but an overestimate of the influence of STT in the
NH may also still contribute to the model–observation differ-
ence in the IH gradient.

Using a combination of aircraft profiles (NOAA flights)
and surface sites (NOAA and AGAGE networks), we have
compared the modelled and observed N$_2$O seasonal cycles
from the surface to the upper troposphere and the CFC-12
and SF$_6$ seasonal cycles at the surface. We found that all
models that simulated CFC-12 accurately matched the phase
and amplitude of the CFC-12 cycle at MHD and were only
circa 1 month out of phase at BRW. In contrast, modelled
N$_2$O seasonal cycles were all 2–3 months out of phase at
both sites. The model–observation mismatch in the N$_2$O sea-
nonal cycle at NH sites is, thus, likely not to be due to errors
in atmospheric transport, which on the basis of the CFC-12
comparison are in the order of the measurement precision
(i.e. 0.1 ppb), but rather due to errors in the N$_2$O flux. Ad-
ditionally, when the simulations using the BWM terrestrial
ecosystem fluxes (as opposed to OCN) were compared, a
much better agreement with the observations was found for BRW, MHD, THD and MLO. While the BWM fluxes have no seasonal component, OCN predicts a late summer maximum. Even after considering the seasonality of STT, a late summer maximum in the surface \( \text{N}_2\text{O} \) fluxes in the mid-to-high northern latitudes is inconsistent with observations. Late summer emissions are likely overestimated in OCN, while emissions in spring and autumn are likely underestimated. Furthermore, the timing of the \( \text{N}_2\text{O} \) mixing ratio minimum in the upper troposphere in the extra-tropical northern latitudes (in June–July) occurs too late to be predominantly due to the winter maximum in diabatic STT i.e. driven by the Brewer–Dobson circulation as previously suggested (Nevison et al. 2007, 2011), but rather is consistent with the effect of increasing tropopause height in spring (Schoeberl, 2004). This spring maximum in mass transfer, convoluted with the seasonality of \( \text{N}_2\text{O} \) loss in the stratosphere and the lag time for this signal to be transported in the troposphere (circa 2 months) more likely explains the phase of the observed signal.

In the southern low latitudes, at SMO, the influence is mostly from IH transport as previously found for \( \text{SF}_6 \) (Denning et al., 1999; Prinn et al., 2000) and \( \text{N}_2\text{O} \) (Nevison et al., 2007; Nevison et al., 2011), while in the SH mid-to-high latitudes, CGO and SPO are strongly influenced by STT and weakly influenced by meridional transport and ocean surface fluxes, as previously shown (Park et al., 2012). The error at these sites due to transport is significant for all models, and thus will result in errors in the seasonality and, with seasonal dependence of atmospheric transport, in the location of emissions estimated from atmospheric inversions.

To conclude, the comparison of modelled and observed \( \text{N}_2\text{O} \) mixing ratios has been shown to provide important constraints on the broad spatial distribution of \( \text{N}_2\text{O} \) emissions and, in the NH, on their seasonality. However, modelled \( \text{N}_2\text{O} \) mixing ratios are sensitive to non-random model transport errors, particularly in the magnitude of STT, which will contribute to errors in \( \text{N}_2\text{O} \) emissions estimates from atmospheric inversions. In the SH mid-to-high latitudes, the influence of transport errors on modelled \( \text{N}_2\text{O} \) mixing ratios is even more important, again largely due to errors in STT, and means that current estimates of seasonality and, to some extent, the location of \( \text{N}_2\text{O} \) emissions in the SH from atmospheric inversions may not be reliable.

Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/14/4349/2014/acp-14-4349-2014-supplement.pdf.

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