

1 TransCom N₂O model inter-comparison Part II: Atmospheric 2 inversion estimates of N₂O emissions

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36 37 38 **Abstract**

39 This study examines N₂O emission estimates from 5 different atmospheric inversion
40 frameworks based on chemistry transport models (CTMs). The 5 frameworks differ in the
41 choice of CTM, meteorological data, prior uncertainties and inversion method but use the
42 same prior emissions and observation dataset. The posterior modelled atmospheric N₂O mole
43 fractions are compared to observations to assess the performance of the inversions and to help
44 diagnose problems in the modelled transport. Additionally, the mean emissions for 2006 to
45 2008 are compared in terms of the spatial distribution and seasonality. Overall, there is a good

1 agreement among the inversions for the mean global total emission, which ranges from 16.1
2 to 18.7 TgN yr⁻¹ and is consistent with previous estimates. Ocean emissions represent
3 between 31% and 38% of the global total compared to widely varying previous estimates of
4 24% to 38%. Emissions from the northern mid to high latitudes are likely to be more
5 important, with a consistent shift in emissions from the tropics and subtropics to the mid to
6 high latitudes in the northern hemisphere; the emission ratio for 0° - 30°N to 30° - 90°N
7 ranges from 1.5 to 1.9 compared with 2.9 to 3.0 in previous estimates. The largest
8 discrepancies across inversions are seen for the regions of South and East Asia and for
9 tropical and South America owing to the poor observational constraint for these areas and to
10 considerable differences in the modelled transport, especially inter-hemispheric exchange
11 rates and tropical convective mixing. Estimates of the seasonal cycle in N₂O emissions are
12 also sensitive to errors in modelled stratosphere-to-troposphere transport in the tropics and
13 southern extra-tropics. Overall, the results show a convergence in the global and regional
14 emissions compared to previous independent studies.

15

16 **1. Introduction**

17 Nitrous oxide (N₂O) currently has the third largest contribution to net radiative forcing after
18 CO₂ and CH₄, and currently has radiative forcing of 0.17 Wm⁻² (Myhre et al., 2013).
19 Furthermore, N₂O plays an important role in stratospheric ozone loss and currently the ozone-
20 depleting-potential weighted emissions of N₂O are thought to be the highest of any ozone-
21 depleting substance (Ravishankara et al., 2009). The atmospheric mole fraction of N₂O has
22 increased significantly since the mid-20th century largely as a result of agricultural activities
23 and, in particular, the use of nitrogen fertilizers (Park et al., 2012). Currently, agricultural
24 emissions from fertilizer use and manure management (4.3 – 5.8 TgN yr⁻¹) and emissions
25 from natural soils (6 – 7 TgN yr⁻¹) account for 60 – 70% of global N₂O emissions (Syakila
26 and Kroeze, 2011; Zaehle et al., 2011). The remaining 30 – 40% of emissions is from oceans
27 (4.5 TgN yr⁻¹) (Duce et al., 2008) and, to a smaller extent, from fuel combustion, industry
28 (Olivier et al., 2005) and biomass burning (together 1.7 TgN yr⁻¹) (van der Werf et al., 2010).

29

30 N₂O is dominantly produced by microbial processes in soils, sediments and water bodies,
31 specifically, by nitrification and denitrification. Although a lot is already known about these
32 processes from laboratory studies under controlled conditions and in-situ chamber flux
33 measurements, up-scaling to emissions on national or regional scales is hampered by the
34 strongly variable nature of soil fluxes. N₂O production in soils is dependent on a multitude of

1 environmental factors such as soil moisture and temperature, soil type, among others, which
2 interact in complex ways, which are difficult to predict (Butterbach-Bahl and Dannenmann,
3 2011). In agricultural soils, the type of nitrogen fertilizer and the timing of its application are
4 also important considerations for estimating N₂O emissions. In natural soils, there is a natural
5 nitrogen turnover leading to N₂O emissions but these may be enhanced by the input of
6 reactive nitrogen from fertilizers and other anthropogenic sources by atmospheric transport,
7 erosion, and leaching, leading to so-called indirect anthropogenic emissions (Galloway et al.,
8 2003).

9
10 An alternative and complementary approach to up-scaling small-scale fluxes and processes to
11 estimate regional and global N₂O budgets, is to use a top-down approach. Atmospheric
12 inversion is one such top-down approach and uses observations of N₂O mole fractions with a
13 model of atmospheric transport and chemistry in a statistically rigorous way to constrain
14 surface fluxes. This approach has been used previously for estimating N₂O emissions on
15 regional (Corazza et al., 2011; Thompson et al., 2011b) and global scales (Hirsch et al., 2006;
16 Huang et al., 2008; Kort et al., 2011; Prinn et al., 1990; Saikawa et al., 2013; Thompson et al.,
17 2014a). One major advantage of the atmospheric inversion approach is that it provides a
18 constraint on the total N₂O emission since the atmosphere integrates the fluxes and requires
19 that the change in atmospheric N₂O abundance be balanced by the sum of its sources and
20 sinks. In general terms, up-scaling approaches provide a detailed picture of the processes and
21 source types while top-down approaches provide an integrated picture of the regional and
22 long-term emissions and a check on the total budget. However, atmospheric inversions also
23 have sources of error. The estimated fluxes are sensitive to errors in the modelled transport
24 and, to varying degrees, the chemistry, as these are non-random errors that are extremely
25 difficult to estimate and account-for in an inversion framework. Particularly for N₂O, errors in
26 stratosphere-troposphere exchange (STE) represent an important source of model error since
27 there is a strong N₂O mole fraction gradient across the tropopause owing to the loss of N₂O
28 through photolysis and reaction with O(¹D) in the stratosphere (see Part I, Thompson et al.,
29 2014b).

30
31 Part I of the TransCom N₂O experiment examined the importance of atmospheric transport
32 and surface fluxes on tropospheric N₂O mole fractions and, specifically, looked at the
33 influence of transport model errors on N₂O mole fractions on seasonal to annual timescales
34 (Thompson et al., 2014b). In this paper (Part II), we present N₂O emission estimates from 5

1 inversion frameworks based on 5 different atmospheric chemistry transport models (CTMs),
2 all of which also participated in Part I. In this context, the objectives of this paper are to:

3

- 4 - compare the posterior emissions (i.e. resulting from the inversion) from all inversions
5 in a standardized way
- 6 - analyse the posterior emissions in terms of spatial distribution, seasonal variability,
7 and to identify robust features common to all inversions
- 8 - identify regions where there are discrepancies between inversions and investigate their
9 cause
- 10 - present regional emissions estimates and their uncertainties

11

12 This paper is divided into four main sections. In section 2, we outline the inversion
13 frameworks and CTMs, as well as the prior flux estimates and atmospheric observations used
14 in this study. Section 3.1 presents a validation of the inversion results by comparing the mole
15 fractions simulated using the posterior fluxes with observations while section 3.2 analyses the
16 spatial and temporal distribution of the posterior fluxes. In section 3.3, we compare these
17 estimates with those of previous studies and conclude with a discussion of the major
18 challenges for estimating N₂O emissions from atmospheric inversions.

19

20 **2. Methods**

21 **2.1. Inversion frameworks**

22 Five different inversion frameworks participated in Part II of this experiment. In this paper,
23 we refer to each of the frameworks according the CTM used followed by “-I” to indicate that
24 this is the inversion framework. Although the frameworks may be used with a different CTM,
25 in this study the naming is unambiguous as a different CTM was used with each one (see
26 Table 1). All frameworks use the Bayesian inversion method to find the optimal surface
27 fluxes, that is, the fluxes that provide the best fit to the atmospheric observations, \mathbf{y} , while
28 being guided by the prior flux estimates, \mathbf{x}_b , and their uncertainties (for details about the
29 Bayesian method refer to (Tarantola, 2005)). Based on Bayesian theory, and Gaussian-error
30 hypotheses, the optimal fluxes are those that minimize the cost function:

31

$$32 \quad J(\mathbf{x}) = (\mathbf{x} - \mathbf{x}_b)^T \mathbf{B}^{-1} (\mathbf{x} - \mathbf{x}_b) + (H(\mathbf{x}) - \mathbf{y})^T \mathbf{R}^{-1} (H(\mathbf{x}) - \mathbf{y}) \quad (1)$$

33

1 where the prior flux uncertainties are described by the error covariance matrix, \mathbf{B} , the
 2 observation uncertainties are described by the error covariance matrix, \mathbf{R} , and H is an operator
 3 of the atmospheric transport and chemistry as defined by the CTM in each inversion
 4 framework. Depending on the inversion framework, H is either a matrix or a non-linear
 5 operator. The frameworks differ in how the minimum of the cost function (Eq. 1) is sought.
 6 Approaches for finding the \mathbf{x} that minimises this equation fall into one of the following
 7 categories: 1) variational methods, such as those used in weather forecasting (Courtier et al.,
 8 1994) and 2) analytical methods (Tarantola, 2005). Variational methods find the optimal \mathbf{x}
 9 using an iterative descent algorithm, usually requiring calculation of the gradient of J at each
 10 iteration and do not require H to be a matrix operator (Chevallier et al., 2005). Analytical
 11 methods require that the transport operator H is linear and defined (i.e. \mathbf{H}) and the optimal
 12 (posterior) \mathbf{x} is found by solving Eq. 2 or 3 directly (for a derivation of these equations refer
 13 to (Tarantola, 2005)):

14

$$15 \quad \mathbf{x} = \mathbf{x}_b + (\mathbf{H}^T \mathbf{R}^{-1} \mathbf{H} + \mathbf{B}^{-1})^{-1} \mathbf{H}^T \mathbf{R}^{-1} (\mathbf{y} - \mathbf{H} \mathbf{x}_b) \quad (2)$$

$$16 \quad \mathbf{x} = \mathbf{x}_b + \mathbf{B} \mathbf{H}^T (\mathbf{H} \mathbf{B} \mathbf{H}^T + \mathbf{R})^{-1} (\mathbf{y} - \mathbf{H} \mathbf{x}_b) \quad (3)$$

17

18 (Analytical methods can also be used in the case that H is non-linear if it is still differentiable
 19 and that the linear \mathbf{H} can be defined over a small range of \mathbf{x} , in which case, an outer loop is
 20 also required to better approximate \mathbf{H}). For inversions falling into the first category, an
 21 adjoint model of the atmospheric chemistry and transport is used to calculate the gradient and
 22 to find the minimum; the TM5-I, TM3-I, and LMDZ4-I frameworks fall into this category
 23 (see Table 2). For inversions in the second category, the chemistry-transport operator, \mathbf{H} ,
 24 represents the sensitivity of the observations to the fluxes in each of a given number of
 25 predefined regions. Each column of \mathbf{H} can be found by running the CTM, perturbing the
 26 fluxes in a given region, and determining the resulting change atmospheric mole fraction for
 27 all observations. The emissions sensitivity is thus the ratio of the change in mole fraction to
 28 the change in flux; the ACTMt42l67-I and MOZART4-I frameworks fall into this category
 29 (see Table 2).

30

31 **2.2. Experiment protocol**

32 As in Part I, all participants were requested to use the same atmospheric observations, prior
 33 flux estimates and approximate magnitude of the stratospheric sink. Thereby, the sources of

1 differences between inversion results are limited to the choice of CTM and meteorological
2 data, the inversion method, and uncertainties assigned to the prior fluxes and the observations.
3 Furthermore, since the CTMs used in each of the inversion frameworks are the same as those
4 used in Part I, the analysis of the transport model performance can be directly applied in this
5 study when considering differences between posterior fluxes. All inversions were run for the
6 period 2005 – 2009 but only output from 2006 onwards was analysed as 2005 was used as a
7 spin-up year. A spin-up period is required to minimize the influence of the initial conditions
8 on the posterior emissions. Here, we chose 1-year for the spin-up as all models started with
9 their best initial conditions estimates established after previous longer integrations of the
10 CTMs. Also, when presenting mean emission results, the years 2006 – 2008 are used, as the
11 end of 2009 is not as well constrained in the inversions (to constrain the end of 2009,
12 observations at the beginning of 2010 would need to be included and these were not all available
13 at the time of preparing this study). .

14

15 **2.2.1. Stratospheric N₂O loss**

16 Loss of N₂O in the stratosphere through photolysis (circa 90% of the loss, (Minschwaner et
17 al., 1993)) and reaction with O(¹D) (circa 10%) was calculated in each model in every grid-
18 cell and time-step. Although the exact photolysis and oxidation rates varied between models
19 (according to the CTM used to calculate the photolysis rate and O(¹D) concentration) these
20 were scaled such that the global annual total loss of N₂O was approximately 12.5 TgN,
21 consistent with estimates of the atmospheric abundance and the lifetime of N₂O, which is
22 estimated to be between 124 and 130 years (Prather et al., 2012; Volk et al., 1997).

23

24 **2.2.2. Prior fluxes**

25 The prior N₂O flux was comprised from estimates of the different sources, that is, from soils
26 (including both natural and agricultural soils), ocean, biomass burning, waste, fuel
27 combustion and industry (see Table 3). For soil fluxes, we used the terrestrial biosphere
28 model, O-CN (Zaehle and Friend, 2010), which is driven by reconstructed observed climate
29 (CRU-NCEP, Climate Research Unit – National Centre for Environmental Prediction), N-
30 fertiliser application, and atmospheric N-deposition data and provides inter-annually varying
31 estimates at monthly and 3.75° × 2.5° (longitude by latitude) resolution as described in Zaehle
32 et al. (2011). For the ocean flux, we used the Pelagic Interaction Scheme for Carbon and
33 Ecosystem Studies (PISCES) ocean biogeochemistry model (Dutreuil et al., 2009), which
34 provides inter-annually varying fluxes at monthly and 1.0° × 1.0° resolution. For waste, fuel

1 combustion, and industrial emissions, we used EDGAR-4.1 (Emission Database for
2 Greenhouse gas and Atmospheric Research, available at:
3 <http://edgar.jrc.ec.europa.eu/index.php>), which are estimated for the reference year 2005 and
4 were provided annually at $1.0^\circ \times 1.0^\circ$ resolution. Biomass burning estimates from GFED-2.1
5 (Global Fire Emissions Database) (van der Werf et al., 2010) were used, which were provided
6 monthly and at $1.0^\circ \times 1.0^\circ$ resolution. In total, the global emission for 2005 to 2009 was 16.8,
7 16.3, 16.8, 16.2 and 16.4 TgN yr⁻¹, respectively.

8

9 **2.2.3. Uncertainty estimates**

10 The prior flux uncertainties were determined following the method usually used for the
11 respective frameworks. For TM5-I, the uncertainties were calculated for each grid cell as
12 100% of the annual mean prior value. For LMDZ4-I, the uncertainties were chosen for each
13 grid cell as 100% of the maximum of the 8 surrounding grid cells plus the one of interest.
14 These were used to form the variances and the square root of total of the prior error
15 covariance matrix was scaled to be equal to 2 TgN yr⁻¹. For TM3-I the uncertainties of the
16 prior flux were calculated as 100% of the flux per grid cell and month. Lastly, for
17 ACTMt42l67-I and MOZART4-I, the regional uncertainty was chosen to be 100% and 50%,
18 respectively, of the regional emission.

19

20 Similarly, each inversion framework has a different estimation method for the representation
21 uncertainty, that is, the uncertainty due to the modelled transport and the temporal
22 representation uncertainty. The transport uncertainties are calculated as follows: TM5-I and
23 LMDZ4-I use the method of Bergamaschi et al., 2010; TM3-I uses pre-determined values for
24 the uncertainty at marine (1.6 ppb), mountain (2.4 ppb), continental (4.8 ppb), and coastal (2.4
25 ppb) locations; MOZART4-I uses the gradient of the monthly mean mixing ratio between the
26 grid cell where the observation site is located and the 8 surrounding grid cells; and
27 ACTMt42l67 uses the 3D gradient (using the 4 horizontal and 2 vertical grid cells)
28 surrounding the observation site. The temporal representation uncertainties are calculated as
29 follows: TM5-I and LMDZ4-I assimilate afternoon/nighttime mean mixing ratios for low
30 altitude/mountain sites, respectively, and use the standard deviation of the afternoon/night
31 mean mixing ratio at each site; MOZART4-I assimilates the monthly mean mixing ratio and
32 uses the standard error of the monthly mixing ratio at each site; ACTMt42l67 also assimilates
33 the monthly mean mixing ratio and uses the standard error of the monthly mixing ratio
34 multiplied by a factor of 2 to account for the underestimation of the variability in the model;

1 and TM3-I assimilates the weekly mean mixing ratio but does not include an estimate of the
2 temporal representation uncertainty.

3

4 **2.2.4. Degrees of freedom**

5 The number of degrees of freedom in the inversion is an important factor for determining how
6 closely the posterior fluxes resemble the prior ones. For MOZART4-I and ACTMt42167-I,
7 which solve the inversion using coarse regions, the number of degrees of freedom is
8 substantially reduced representing a strong constraint on the inversion as only the mean flux
9 in each region is optimized and the flux pattern within each region remains as described a
10 priori. On the other hand, solving for fine regions i.e. at the resolution of the transport model,
11 as in TM5-I, TM3-I and LMDZ4-I, benefits from additional regularization constraints, such
12 as spatial correlations of the prior flux errors (used in the definition of **B**). For TM5-I the
13 spatial correlation length (200 km) means that the grid cells are only weakly correlated to one
14 another resulting in a weak constraint, whereas in LMDZ4-I, longer scale lengths are used
15 (500 km for land and 1000 km for ocean) resulting in a stronger constraint (see Table 2).

16

17 **2.3. Atmospheric observations**

18 Atmospheric observations of N₂O mole fractions (nmol mol⁻¹ equivalently parts-per-billion,
19 abbreviated as ppb) were pooled from two global networks, NOAA CCGG (Carbon Cycle
20 and Greenhouse Gases) and AGAGE (Advanced Global Atmospheric Gases Experiment), as
21 well as from a number of smaller regional networks and independent stations (see Fig. 1 and
22 Table 4). From the NOAA CCGG network, 42 sites were included. Approximately weekly
23 discrete air samples are taken at these sites, which are subsequently analysed for N₂O using
24 GC-ECD (Gas Chromatography Electron Capture Detector). These data are reported on the
25 NOAA-2006A calibration scale (Hall et al., 2007) and have a reproducibility of 0.4 ppb based
26 on the mean difference of flask pairs. The AGAGE network consists of 5 in-situ GC-ECD
27 instruments. These data are reported on the SIO-1998 scale and have a reproducibility of
28 approximately 0.1 ppb (Prinn et al., 2000). The MPI-BGC (Max Planck Institute for
29 Biogeochemistry) network consists of 3 sites for discrete air samples and 2 sites with in-situ
30 GC-ECD instruments. These data are also reported on the NOAA-2006A scale and have a
31 reproducibility of about 0.3 ppb. In addition, data from 9 independently run stations with in-
32 situ GC-ECD instruments were included (see Table 4).

33

1 These stations do not all use the same calibration scale and, thus, offsets exist between the
2 measurements. Furthermore, even in the case where the measurements are reported on the
3 same scale, there still may be offsets owing to systematic errors. These offsets can introduce
4 significant errors in the optimized fluxes if they are not accounted for prior to, or in, the
5 inversion. For this reason, calibration offsets were estimated using inter-calibration data for
6 each of the in-situ stations, and for the 3 MPI-BGC flask sites together, relative to the NOAA-
7 2006A scale (see Table 5). Since the inter-calibration data were not complete for all times and
8 all sites, the offsets were included into the optimization problem in inversion frameworks
9 with this capacity (i.e. in LMDZ4-I and TM5-I, and only TM5-I resolves the offsets
10 temporally using annual resolution). In this case, the best estimates of the offsets were used as
11 prior values. In the case that they could not be optimized (i.e. in MOZART4-I, ACMTt42l67-
12 I, and TM3-I) the given values were used to correct the observations prior to the inversion.

13

14 **3. Results and Discussion**

15 **3.1. Validation with atmospheric observations**

16 **3.1.1. Meridional gradients**

17 Meridional gradients are some of the most commonly used observational parameters to assess
18 CTMs, as they provide a constraint on features such as inter-hemispheric transport and
19 latitudinal flux distributions (Gloor et al., 2007; Patra et al., 2011). Figure 2 shows the
20 observed annual mean meridional mole fractions (2006 to 2009) compared with simulations
21 by each CTM integrated with the corresponding posterior fluxes. For both the observations
22 and the simulations, the gradients were calculated from detrended and deseasonalized N₂O
23 mole fractions at background surface sites. For each model, a very good agreement was found
24 with the gradient derived from surface observations (correlation coefficient $R^2 \geq 0.9$ for each
25 model). In MOZART4-I, the mean mole fraction is approximately 1.5 ppb higher, which is
26 most likely due to too high mole fractions in the initial conditions (see also Fig. S1), but it
27 still captures the gradient reasonably well.

28

29 Gradients in the pressure-weighted column mean N₂O were also compared against
30 observations from HIPPO (Hiaper Pole-to-Pole Observations, <http://hippo.ucar.edu>)
31 campaigns in January and November 2009 (Fig. 3). In contrast to the surface, the simulations
32 all underestimate the total column inter-hemispheric gradient in January by about 1 ppb (circa
33 50%). In November, the inter-hemispheric gradient is smaller and is matched more closely by
34 the models; however, there is an overall offset of about 1 ppb (except MOZART4-I where its

1 1.5 ppb offset compensates). The offset in November may be in part due to a calibration
2 difference between HIPPO and the NOAA data, which were used in the inversion, as
3 comparisons of the HIPPO data between 0 and 2000 m around 19°N and 14°S with the
4 NOAA data at Mauna Loa (19.5°N, 155.6°W) and Samoa (14.3°S, 170.6°E), respectively,
5 show an offset of about 0.5 ppb. The underestimate of the gradient in January may be due to
6 the models underestimating N₂O mole fractions in the upper troposphere as the agreement
7 with the observed column is much better up to 2000 m, within a few tenths of a ppb (except
8 north of about 50°N) (Fig. S2). Kort et al. (2011) obtained a similar result when they
9 assimilated only surface data (i.e. within 250 – 750 m above sea level) from the HIPPO
10 campaigns, finding that the simulations using the optimized fluxes underestimated the column
11 mean N₂O but if the total column was assimilated, larger tropical fluxes were obtained and
12 the total column matched the observations. Kort et al. (2011) reasoned that this was because
13 the surface network failed to detect high N₂O signals in the tropics and that these were lofted
14 to higher altitudes with strong tropical convection. If the fluxes in this study were
15 underestimated for this reason, then this would result in a too low growth rate of N₂O in the
16 troposphere. However, all models capture the observed growth rate within 0.17 ppb yr⁻¹
17 (20%) and most within 0.1 ppb yr⁻¹ (10%) (Fig. S3). The simulated upper troposphere values
18 of N₂O in January may also be underestimated due to model transport errors such as too
19 strong STE as was suggested in Part I of the inter-comparison (Thompson et al., 2014b),
20 which would be much more apparent in the mole fractions above the planetary boundary layer
21 (PBL) and is consistent with what we find in the comparisons up to 2000 m versus up to
22 10000 m. If this were the case, and if no bias correction were applied to account for the
23 transport error, then assimilating observations in the upper troposphere may lead to a
24 systematic overestimate of the emissions.

25

26 **3.1.2. Seasonal cycles**

27 In Part I of the inter-comparison, considerable attention was paid to the seasonal cycle of N₂O
28 as this is sensitive to STE, the height of the PBL, inter-hemispheric mixing, and seasonality in
29 the fluxes. Figure 4 shows the annual mean (2006 to 2009) seasonal cycles from the posterior
30 model simulations and observations at 6 key background sites. In the NH mid to high
31 latitudes, i.e. at MHD and BRW, the phase and amplitude are reasonably well captured by
32 ACTMt42l67-I, TM5-I and LMDZ4-I with a minimum occurring in August, whereas
33 MOZART4-I and TM3-I simulate a too early minimum at both sites by up to 2.5 months, as
34 was also the case for all CTMs a priori. However, all 5 CTMs participating in Part II were

1 able to capture the correct phase when using an alternative prior flux estimate with no
2 terrestrial biosphere seasonal cycle (see Part I, Thompson et al., 2014b) suggesting that the
3 reason for the too early minimum was not related to transport problems but rather to the
4 seasonality in the fluxes. This also seems to be the case for MOZART4-I and TM3-I, which
5 have the smallest shift in the seasonal cycle relative to the prior fluxes (this is discussed in
6 more detail in Section 3.2.3). At MLO, all CTMs simulate a too early minimum as was also
7 the case using the a priori emissions. However, with the a posteriori emissions, the amplitude
8 is closer to that observed. The timing of the minimum, in April, in the models is consistent
9 with the expected maximum influence of stratospheric air in the troposphere owing to the
10 downward branch of the Brewer Dobson circulation, which has a maximum in December to
11 February in the NH. However, the fact that the observed minimum occurs later may suggest
12 that the influence of stratosphere to troposphere transport (STT) is overestimated in the
13 models and/or that the seasonality is still not correct in the fluxes at the latitude of MLO.

14

15 For the Southern Hemisphere sites, SMO and CGO, all models agree well with the observed
16 seasonal cycles except MOZART4-I at SMO and TM3-I at CGO. At SPO, however, all
17 models underestimate the amplitude and MOZART4-I and TM3-I are also out of phase. It has
18 been shown with N₂O isotope measurements that the seasonality at CGO is determined by the
19 combined influences of STT and ocean fluxes leading to the observed minimum in April
20 (Park et al., 2012). With the a priori fluxes, both TM3-I and LMDZ4-I had the phase of the
21 seasonal cycle at CGO out by nearly 6 months indicating a problem with STT in the Southern
22 Hemisphere (see Thompson et al., 2014b). A similar error in MOZART4-I was observed at
23 SPO as well. However, a posteriori, LMDZ4-I has a much-improved fit to the phase at CGO
24 and SPO, which was achieved by increasing the amplitude of the flux seasonality in the
25 Southern Ocean, whereas TM3-I and MOZART4-I make nearly no adjustment (this is
26 discussed further in Section 3.2.3).

27

28 **3.2. Comparison of posterior emissions**

29 In this section, we present a comparison of the posterior emission estimates. All posterior
30 emissions were compared after they were interpolated from the corresponding model grid to
31 1°×1° resolution.

32

33 **3.2.1. Global means**

1 Table 6 shows the global total emission a priori and the global total emission and sink a
2 posteriori calculated by each inversion framework. On the basis of the posterior emissions,
3 the inversions can be grouped into two categories: 1) those with low global totals, i.e.
4 MOZART4-I, ACTMt42l67-I and TM3-I and 2) those with high global totals, i.e. TM5-I and
5 LMDZ4-I, where low and high are defined relative to the prior. In the case of MOZART4-I,
6 the low global total (the lowest of all inversions) results from the overestimate of N₂O mole
7 fractions in the initial conditions, which leads to the emissions being underestimated and a too
8 low atmospheric N₂O growth rate (see Fig. S3). For this reason, the MOZART4-I estimates
9 are not included further in the flux totals. However, in general, the low/high categorisation
10 also corresponds to how the observations were assimilated in the inversion; the first category
11 inversions assimilate monthly (MOZART4-I and ACTMt42l67-I) or weekly (TM3-I) means,
12 while those in the second category (TM5-I and LMDZ4-I) use the afternoon means for sites
13 within the PBL and nighttime means for mountain sites. This feature of the category 2
14 inversions means that they are also sensitive to the synoptic variability of the observations,
15 while in the category 1 inversions this signal is smoothed-out. Furthermore, the category 1
16 inversions may overestimate the monthly/weekly mean N₂O mole fraction a priori as
17 compared to the NOAA CCGG flask measurements, since the flask samples are generally
18 collected during meteorological conditions corresponding to background air, whereas in the
19 model, it is the monthly/weekly mean of all data. MOZART4-I and ACTMt42l67-I, which
20 have the lowest global total estimates, also differ from the other inversions in that they solve
21 for emissions in large regions as opposed to solving the emissions at the resolution of the
22 transport model. All inversion frameworks had very similar global total sinks, within less than
23 1 TgN yr⁻¹ of each other for each year, thus differences in the calculated loss rate is not a
24 reason for the differences in global total emissions.

25

26 Overall the global distribution of N₂O emissions was similar in all inversions and close to that
27 a priori (Fig. 5). The highest emissions were found in the subtropical and tropical regions of
28 South America, Africa and Asia, in Europe and the eastern states of the USA. However, the
29 inversions differ in the relative importance of emissions in each of these sub-continental
30 regions. Figure 6 shows the annual mean flux increments made by each inversion, i.e. the
31 posterior minus prior annual mean flux. There are a number of features in the increments that
32 are common to all inversions: 1) lower (relative to the prior) emissions in temperate land
33 regions in the SH, 2) higher emissions in central Europe, 3) higher emissions in central Africa
34 and 4) no significant change in northern Eurasia and Canada. On the other hand, the

1 inversions differ significantly in the direction and/or magnitude of the flux increments for the
2 USA (eastern states), South and East Asia, and tropical South America. This information is
3 summarized in Fig. 7, which shows the median absolute deviation (MAD) of the annual mean
4 emissions from all 5 inversions. Regions with highest MAD correspond to regions with the
5 greatest discrepancy among the inversions.

6

7 To better examine the differences between the a posteriori emissions, we compare the annual
8 mean zonally integrated emissions plotted against latitude and the accumulated emissions
9 from south to north (Fig. 8). By plotting the emissions in this way, differences in the
10 latitudinal distribution of the emissions are more apparent and may be assessed in terms of
11 different features of the CTMs used in the inversions, such as the rate of inter-hemispheric
12 and vertical mixing. Moving from south to north, one can see that all inversions estimate
13 lower emissions compared to the prior in the Southern Hemisphere; it is only north of the
14 Equator that some of the inversions have a higher accumulated emission. TM5-I has the
15 highest emission estimate for the Southern Hemisphere tropics and is also the most southern
16 crossing point with the prior accumulated emissions. This is likely related to the fact that
17 TM5-I has a long inter-hemispheric exchange time (1.7 years compared to the observed 1.4
18 years in 2006, based on SF₆ mole fractions at BRW, MLO, CGO and SPO (Patra et al.,
19 2011)), which would mean that in order to match the observed atmospheric N₂O mole fraction
20 in the Southern Hemisphere tropics, higher emissions in this region are required. It can be
21 expected that TM5-I would also for this reason estimate lower emissions in the Northern
22 Hemisphere tropics and sub-tropics, however, the accumulated emissions still exceed those of
23 e.g. LMDZ until circa 30°N. The reason for this cannot be determined from these results
24 alone but it may be at least in part also owing to transport errors in LMDZ. At circa 30°N,
25 LMDZ4-I surpasses both the prior and TM5-I accumulated emissions owing to very large
26 emission estimates in the Northern Hemisphere sub-tropics. LMDZ4-I (in the present 19-layer
27 configuration) has a relatively short inter-hemispheric exchange time, 1.2 years in 2006 (Patra
28 et al., 2011), and has been found to have a very diffusive PBL in the Northern Hemisphere
29 mid latitudes (Geels et al., 2007). These features likely lead to too high emissions in the
30 northern sub-tropics and mid latitudes. North of circa 50°N, the zonally integrated emission
31 differs very little among the inversions and the prior, however, the accumulated total emission
32 at 90°N differs owing to the aforementioned disparities.

33

34 **3.2.2. Regional means**

1 Figure 9 shows the annual mean total emissions for 7 sub-continental and 3 ocean regions
2 from each of the inversions and the prior, in addition, the corresponding range, median, and
3 MAD of the emissions, as well as the uncertainty calculated from a single inversion model
4 (LMDZ-I), are given in Table 7. The calculated uncertainties per region are larger than the
5 corresponding MAD values indicating that the spread of posterior emissions is smaller than
6 the uncertainty calculated for a single inversion. For only 3 out of the 7 land regions is there a
7 significant change in emissions with respect to the prior. Here, we define significant to mean
8 that: 1) all inversions agree on the direction of the change and 2) the prior value is outside the
9 range of the posterior median and plus or minus MAD. These regions are Africa, Europe and
10 Australasia. For Australasia, the contribution to the global total (2%, median posterior value)
11 and the absolute change relative to the prior (0.08 TgN yr^{-1}) are very small, and thus this
12 region is not discussed further. Europe was found to have 30% (0.24 TgN yr^{-1}) higher
13 emissions than estimated a priori and contributes on average 6% (median posterior value) to
14 the global total emission. Africa was also found to have higher emissions relative to the prior
15 (by 10%, equivalent to 0.29 TgN yr^{-1}) and contributes on average 20% to the global total
16 emission. Of the regions where the change was not considered significant, North America as
17 well as South and Tropical America still satisfied the second criterion. For North America, all
18 inversions except LMDZ4-I estimated lower emissions (by 26%, equivalent to 0.26 TgN yr^{-1})
19 bringing its contribution to the global total to 4%, and for South and Tropical America, all
20 inversions except TM5-I estimate lower emissions (by 9%, equivalent to 0.22 TgN yr^{-1})
21 bringing its contribution to the global total to 14%. For South Asia and North Asia, however,
22 the inversions differed significantly both in the direction of change as well as in the
23 magnitude. While the total emission from North Asia is small (2% of the global) that from
24 South Asia is very important (approximately 17% of the global).

25

26 There are several reasons why the inversions differ so substantially for South Asia. First, this
27 region is not well covered by the observation network. Emissions from this region are only
28 constrained by the 2 in-situ sites, HAT and COI, and by the discrete sampling sites, BKT,
29 GMI, LLN, and TAP. Second, since the prior flux uncertainties are calculated proportionally
30 to the prior flux, the prior uncertainty for this region is large allowing the inversions
31 considerable freedom to adjust the fluxes here. Lastly, differences in the modelled transport,
32 such as the tropical convection, monsoon flow, and shifts in the North Pacific storm track,
33 which are important in determining outflow from the Asian continent (Stohl et al., 2002) may
34 also contribute to the disparity among emission estimates for South Asia. Stohl et al. (2002)

1 showed that tracers emitted in Asia south of 30°N, particularly in India, are readily
2 transported toward the ITCZ and thus could be one reason why LMDZ4-I, with a fast inter-
3 hemispheric mixing rate, predicts the highest emissions for South Asia. Similar reasoning also
4 applies to the large discrepancy for South and Tropical America. South and Tropical America
5 is very poorly covered by the observation network (see Fig. 1) and the prior flux uncertainty
6 for this region is very large. The posterior emission estimates for this region are also likely to
7 be sensitive to features of the modelled transport, in particular, convective transport.

8

9 Unlike for the land regions, there is reasonably good agreement among inversions for the
10 ocean regions. All ocean regions satisfy the second criterion (i.e. the prior value is outside the
11 range of the posterior median and MAD), and only the region 30°S – 30°N does not also
12 satisfy the first criterion (i.e. that all inversions agree on the direction of the change). The
13 emissions for the Southern Ocean (90° – 30°S) were found to be smaller than estimated a
14 priori, contributing 6% (median posterior value) to the global total, while emissions for the
15 tropical (30°S – 30°N) and northern (30° – 90°N) ocean regions, the emissions were found to
16 be larger, contributing 22% and 7% to the global total, respectively.

17

18 **3.2.3. Seasonal variability**

19 The mean seasonal cycle for each of the 7 land and 3 ocean regions was calculated by
20 averaging the total monthly emissions over the period 2006 to 2008 and is shown in Figure
21 10. For the Northern Hemisphere temperate land regions, Europe, North America and North
22 Asia, the prior flux seasonal cycle predicts a late summer maximum, i.e. between July and
23 August. However, all inversions estimate smaller emissions in July and/or August relative to
24 the prior. ACTMt42l67-I and LMDZ4-I both estimate an earlier and broader maximum,
25 between April and June, while MOZART4-I, TM5-I and TM3-I predict a broader maximum
26 between June and July. In Part I of the inter-comparison, it was shown in the CTM
27 integrations using fluxes with a late summer maximum worsened the fit to the atmospheric
28 observations compared to using fluxes with no seasonal cycle. The result for the Northern
29 Hemisphere temperate regions in this study confirms the hypothesis in Part I, that elevated
30 emissions begin in earlier in spring and continue until autumn without a peak in late summer.
31 This is in line with what is expected based on the dependence of N₂O fluxes on soil moisture
32 (measured by water-filled-pore-space, WFPS), soil temperature and the availability of
33 nitrogen substrates, particularly NO₃⁻ and NH₄⁺ in soils (Butterbach-Bahl et al., 2013, and
34 references therein). N₂O flux is maximised with WFPS of between approximately 70 – 90%

1 and has positive correlation with soil temperature (Smith et al., 1998). Therefore, low soil
2 N₂O flux is expected throughout winter and higher N₂O is expected in summer so long as
3 there is sufficient soil moisture and nitrogen substrate. N-fertilization usually occurs in spring
4 and mid-summer providing sufficient nitrogen substrate but drier soils in late summer may
5 limit N₂O fluxes.

6
7 For the region of South Asia, there is some indication in the posterior fluxes of a double
8 maximum, i.e. in ACTMt42l67-I, TM5-I, and LMDZ4-I occurring in April and September.
9 This approximately corresponds to the start and end of the Asian monsoon season, which lasts
10 from April to September, while the period of lowest fluxes, from October to March,
11 corresponds to the cool-dry season. This is in accordance with what has been found from in-
12 situ flux measurements in sub-tropical Southern China, which experiences annual monsoons,
13 that is, that WFPS, soil NO₃⁻ and NH₄⁺ content, and N₂O fluxes were significantly higher in
14 the hot-humid season than in the cool-dry season (Lin et al., 2010). However, the peak in
15 spring may also partially be an artefact needed to compensate for the too low simulated spring
16 atmospheric mole fraction as compared to the observations owing to a too strong influence of
17 STT.

18
19 For the Southern Hemisphere regions of South and Tropical America and Africa, there is very
20 little seasonality in the prior fluxes. However, all of the inversions estimate a March – April
21 minimum for South and Tropical America and similarly (except LMDZ4-I) for Africa. For
22 South and Tropical America, the March – April minimum is not easy to explain in terms of
23 soil N₂O fluxes. In fact, from the few existing regional measurements of N₂O fluxes in
24 tropical South America only a small seasonal cycle has been observed with elevated fluxes
25 during the wet season from March – May (D'Amelio et al., 2009). Therefore, it is likely that
26 the minimum in the optimized fluxes is due to transport errors since the timing of the
27 atmospheric N₂O minimum in April, determined to a large extent by STT, is not captured by
28 the models, thus to match observations, the inversions estimate lower N₂O emissions at this
29 time. It is possible that the impact of this transport error on the optimized fluxes would not be
30 so strong if there were better observational constraints for South America. The same also
31 applies for Africa where the minimum in March – April cannot be explained in terms of
32 variability in soil fluxes as this time corresponds to the wet season when the highest N₂O
33 emissions are expected.

34

1 For the ocean regions, the phase and amplitude of the seasonal cycles a posteriori differ little
2 from that a priori. In the Southern Ocean, the minimum in April and maximum in September
3 – October is consistent with the independent estimate of Nevison et al. (2005) and is largely
4 driven by the upwelling and subsequent venting of subsurface water, which is enriched in
5 N₂O. In LMDZ, however, the amplitude of the seasonal cycle is significantly larger,
6 especially owing to the lower minimum in April, which is most likely also an artifact of the
7 modeled transport. In the tropical and northern ocean regions, the seasonal cycle is much
8 smaller in amplitude but is also likely driven by seasonal changes in upwelling.

9

10 **3.3 Comparison with other estimates**

11 To put this study into context with previous work, we compare our results to independent
12 N₂O emission estimates. We have chosen 5 studies, including 2 atmospheric inversions
13 (Hirsch et al., 2006; Huang et al., 2008) and 3 inventory and model-based estimates (Denman
14 et al., 2007; Syakila and Kroeze, 2011; Zaehle et al., 2011), which are global in coverage and
15 include estimates of N₂O emissions from all sources and are thus appropriate for this
16 comparison. (The study of Zaehle et al. (2011) is not completely independent as it uses the
17 same terrestrial biosphere model, O-CN, for the estimate of N₂O soil emissions as was used in
18 this study's prior emissions, however, the O-CN simulations used different climate forcing
19 and N-deposition.) Figure 11 compares the global, land, and ocean total emissions, as well as
20 the emission distribution by semi-hemisphere, where available. Although the exact period of
21 each study varies, they all include estimates of the global N₂O budget in the 2000s. At the
22 global scale, all estimates agree within the range of uncertainties (no uncertainty estimate was
23 provided by Syakila and Kroeze (2011)). Progress, however, has been made in reducing the
24 level of uncertainty from 4.5 TgN yr⁻¹ in the IPCC AR4 (Intergovernmental Panel on Climate
25 Change Fourth Assessment Report, 2007) to 0.7 TgN yr⁻¹ in this study (1σ, 68% probability
26 assuming Gaussian error distribution) with the complete range of inversions from 16.1 to 18.7
27 TgN yr⁻¹ for the mean 2006 - 2008. Previous studies differ in the apportionment between land
28 and ocean emissions, with ocean estimates varying from 24% to 38% of the global total,
29 whereas we found fairly good agreement among the inversions participating in this study with
30 ocean estimates varying between 31% and 38% of the global total. At the semi-hemisphere
31 scale, we find a few important differences between our median estimates and previous ones:
32 for the region 90°S to 30°S we estimate higher emissions (7% of the global total), for the
33 region 0° to 30°N we estimate lower emissions (41%), and for 30°N to 90°N slightly higher
34 emissions (23%). Comparing the ratio for emissions in the regions 0° to 30°N and 30°N to

1 90°N, all our inversions give a lower value (from 1.5 to 1.9) compared with 3.0 (Hirsch et al.,
2 2006) and 2.9 (Huang et al., 2008) for the periods 1998 – 2005 and 2001 – 2005, respectively.
3 Since our estimates are for a later period (2006 – 2008), this difference may reflect real
4 changes in emissions. It is known that emissions have been increasing in Asia, particularly, in
5 China, over the past decade, which has also increased the overall emission in the region 30°N
6 to 90°N, while no significant trends have been found in other regions (Thompson et al.,
7 2014a). The increase in China has primarily been driven by an increase in N-fertilizer usage
8 and to a lesser extent, an increase in industrial and combustion sources of N₂O (Thompson et
9 al., 2014a).

10

11 **4. Summary and conclusions**

12 In this study we have compared the N₂O emission estimates of 5 inversion frameworks and
13 analysed these in terms of their spatial distribution and seasonal variability. In general, there
14 is a high level of agreement among the 5 inversions participating in this study despite the
15 differences in inversion approach, atmospheric transport model and meteorological data used.
16 This gives us confidence that there has been substantial progress made in terms of uncertainty
17 reduction. Moreover, we have identified emission patterns that are robust, that is, common to
18 all inversion frameworks as well as those that depend strongly on the modelled transport
19 and/or inversion set-up. The salient results are summarized as follows:

20

- 21 - the mean global annual N₂O emission ranges between 16.1 and 18.7 with a median
22 and median absolute deviation (MAD) of 16.7 and 0.7 TgN yr⁻¹, respectively, for the
23 years 2006 to 2008
- 24 - ocean emissions were found to contribute between 31% and 38% and land emissions
25 between 62% and 69% to the global total
- 26 - the apportionment of emissions to each semi-hemisphere was fairly close among
27 inversions, with 7 ± 1% to 90°S - 30°S, 28 ± 2% to 30°S - 0°, 41 ± 1% to 0° - 30°N
28 and 23 ± 1% to 30°N - 90°N (median and MAD as a percentage of the global total),
29 thus making the Northern Hemisphere tropics and subtropics the most important
30 latitudinal range for N₂O emissions globally
- 31 - all inversions estimated lower emissions for the latitudes 90°S - 30°S relative to the
32 prior, however, the median estimate (7% of the global total) was still higher than that
33 found in previous studies (0 to 4%)

- 1 - the ratio of emissions in 0° - 30°N to 30°N - 90°N is smaller in all inversions (range of
2 1.52 to 1.91 and median of 1.9) compared to previous studies (2.9 and 3.0),
3 representing a change in the percentage of the global total of -16% for 0° - 30°N and
4 of +3% for 30°N - 90°N
- 5 - all inversions estimated higher emissions in Europe and Africa relative to the prior,
6 contributing 6% ($1.04 \pm 0.20 \text{ TgN yr}^{-1}$) and 20% ($3.36 \pm 0.04 \text{ TgN yr}^{-1}$) (median and
7 MAD values), respectively to the global total compared with 5% (0.80 TgN yr^{-1}) and
8 18% (3.07 TgN yr^{-1}) a priori
- 9 - all inversions (except LMDZ4) estimate lower emissions in North America
10 contributing 4% ($0.74 \pm 0.11 \text{ TgN yr}^{-1}$) (median values) to the global total compared
11 to 6% (1.00 TgN yr^{-1}) a priori
- 12 - all inversions (except TM5) estimate lower emissions in South and Tropical America
13 contributing 14% ($2.33 \pm 0.27 \text{ TgN yr}^{-1}$) to the global total compared to 15% (2.55
14 TgN yr^{-1}) a priori
- 15 - the largest uncertainties were found in the estimates for South and Tropical America
16 and South Asia owing to uncertainties in the modelled atmospheric transport and to
17 the poor observational constraint for these regions
- 18 - differences in the meridional distribution of emissions among the inversions were also
19 found to depend on the inter-hemispheric mixing rate of the CTMs
- 20 - assimilating monthly mean observations from flask sampling networks most likely
21 leads to an underestimate of the emissions

22

23 In general, the global N_2O budget, the total emissions and their spatial distribution, are close
24 to what has been found from previous studies. One notable difference in our inversion
25 estimates compared to previous ones though, is the shift in the distribution in the Northern
26 Hemisphere, with lower emissions in the tropics and subtropics and higher emissions in
27 temperate latitudes. Moreover, our inversions show a convergence of estimates both at the
28 global and sub-continental scale. This good agreement is most likely due to the expansion of
29 the atmospheric observation network. However, considerable uncertainties remain, especially
30 in the less well-constrained regions of South Asia and South and Tropical America. These
31 regions also appear to be very sensitive to uncertainties in the modelled atmospheric transport
32 and are regions that should be targeted for new observation sites. Also sensitive to
33 atmospheric transport, is the seasonal flux variability. Although this appears to be robust in

1 the northern extra-tropics, for the tropics and southern extra-tropics, this is strongly dependent
2 on having adequate representation of the timing of the maximum in stratosphere to
3 troposphere transport (STT) and in vertical mixing, which is still not the case in most CTMs.
4 However, inter-annual variations in fluxes are likely to be more robust as the year-to-year
5 variations in STT are not as great as the seasonal variations. Improvements in the accuracy of
6 N₂O emission estimates from atmospheric inversions, and to move towards emissions
7 monitoring in the context of the Kyoto Protocol, would require improvements to modelling of
8 atmospheric transport, in particular, STT, which has a strong influence on tropospheric N₂O
9 mole fractions.

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1 Table 1. Overview of the CTMs used in the inversions. Note that the horizontal resolution is
 2 given as longitude by latitude.

Model	Institute	Resolution		Top boundary pressure (hPa)	Meteorology
		horizontal	vertical		
MOZART4	MIT	$2.5^\circ \times 1.88^\circ$	$56 \sigma^1$	2	MERRA
ACTMt42l67	JAMSTEC	$2.8^\circ \times 2.8^\circ$	67σ	0.01	JRA25
TM3	MPI-BGC	$5.0^\circ \times 3.75^\circ$	$26 \eta^2$	1	ERA-interim
TM5	JRC	$6.0^\circ \times 4.0^\circ$	25η	0.5	ERA-interim
LMDZ4	LSCE	$3.75^\circ \times 2.5^\circ$	19η	4	ERA-interim

- 4 1. σ refers to the sigma terrain-following vertical coordinate system.
 5 2. η refers to the eta coordinate system that smoothly transitions from the sigma coordinate
 6 near the surface to a pressure coordinate in the stratosphere.

8 Table 2. Overview of the inversion frameworks. The matrix **B** is the prior flux error
 9 covariance matrix (see Eq. 1).

Model	Resolution		Inversion method	Scale length in B (km)	
	spatial	temporal		land	ocean
MOZART4-I ¹	13 regions	monthly	Analytical	none	none
ACTMt42l67-I ²	22 regions ⁶	monthly	Analytical	none	none
TM3-I ³	$5.0^\circ \times 3.75^\circ$	monthly	Variational	500	500
TM5-I ⁴	$6.0^\circ \times 4.0^\circ$	monthly	Variational	200	200
LMDZ4-I ⁵	$3.75^\circ \times 2.5^\circ$	monthly	Variational	500	1000

- 11 1. (Saikawa et al., 2013)
 12 2. (based on Rayner et al., 1999)
 13 3. (Rödenbeck, 2005)
 14 4. (Corazza et al., 2011)
 15 5. (Thompson et al., 2011a)
 16 6. TransCom-3 regions

18 Table 3. Prior flux model overview (totals shown for 2005).

Category	Dataset	Resolution	Total (TgN y ⁻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		monthly	16.84

20
 21

1 Table 4. Atmospheric observation sites using in the inversions. (F = Flask, C = Continuous).
 2 Altitude is specified as metres above sea-level (masl).
 3

ID	Station	Operator	Type	Latitude	Longitude	Altitude (masl)
ALT	Alert, Canada	NOAA	F	82.5°N	62.5°W	210
ASC	Ascension Isl., UK	NOAA	F	7.9°S	14.4°W	54
ASK	Assekrem, Algeria	NOAA	F	23.2°N	5.4°E	2728
AZR	Azores, Portugal	NOAA	F	38.8°N	27.4°W	40
BAL	Baltic Sea, Poland	NOAA	F	55.4°N	17.2°E	7
BIK	Bialystok, Poland	MPI-BGC	C	55.3°N	22.8°E	460
BKT	Bukit Kototabang, Indonesia	NOAA	F	0.2°S	100.3°E	865
BME	St. Davis Head, Bermuda, UK	NOAA	F	32.4°N	64.7°W	30
BMW	Tudor Hill, Bermuda, UK	NOAA	F	32.3°N	64.9°W	30
BRW	Barrow, Alaska	NOAA	F	71.3°N	156.6°W	11
BSC	Black Sea, Romania	NOAA	F	44.2°N	28.7°E	3
CBA	Cold Bay, Alaska	NOAA	F	55.2°N	162.7°W	21
CBW	Cabauw, Netherlands	ECN	C	52.0°N	4.9°E	118
CGO	Cape Grim, Tasmania	AGAGE	C	40.7°S	144.7°E	164
CHR	Christmas Isl.	NOAA	F	1.7°N	157.2°W	3
COI	Cape Ochi-ishi, Japan	NIES	C	43.2°N	145.5°E	45
CRZ	Crozet Isl., France	NOAA	F	46.45°S	51.9°E	120
CVR	Calhau, Cape Verde	MPI-BGC	F	16.9°N	24.9°W	10
EIC	Easter Island, Chile	NOAA	F	27.2°S	109.5°W	50
GMI	Mariana Isl., Guam	NOAA	F	13.4°N	144.8°E	2
HAT	Hateruma, Japan	NIES	C	24.1°N	123.8°E	10
HBA	Halley Stn., Antarctica	NOAA	F	75.6°S	26.5°W	30
HUN	Hegyhatsal, Hungary	ELTE	C	46.9°N	16.7°E	344
ICE	Heimay, Iceland	NOAA	F	63.3°N	20.3°W	118
IZO	Tenerife, Spain	NOAA	F	28.3°N	16.5°W	2360
JFJ	Jungfrauoch, Switzerland	EMPA	C	46.6°N	8.0°E	3580
KEY	Key Biscayne, Florida	NOAA	F	25.7°N	80.2°W	3
KUM	Cape Kumukahi	NOAA	F	19.5°N	154.8°W	3
KZD	Sary Tauku, Kazakhstan	NOAA	F	44.1°N	76.8°E	601
LEF	Park Falls, Wisconsin	NOAA	F	45.9°N	90.3°W	868
LLN	Lulin, Taiwan	NOAA	F	23.5°N	120.9°E	2867
LUT	Lutjewad, Netherlands	RUG-CIO	C	53.4°N	6.4°E	60
MHD	Macehead, Ireland	AGAGE	C	53.3°N	9.9°W	25
MLO	Mauna Loa, Hawaii	NOAA	F	19.5°N	155.6°W	3397
NWR	Niwot Ridge	NOAA	F	40.0°N	105.5°W	3526
NMB	Gobabeb, Namibia	NOAA	F	23.6°S	15.0°E	456
OXK	Ochsenkopf, Germany	MPI-BGC	C	50.1°N	11.8°E	1185
PAL	Pallas, Finland	FMI	C	68.0°N	24.1°W	560
PSA	Palmer Stn, Antarctica	NOAA	F	64.9°S	64.0°W	10
PTA	Point Arena, California	NOAA	F	39.0°N	123.7°W	55
RPB	Ragged Point, Barbados	AGAGE	C	13.2°N	59.4°W	45
SEY	Mahe, Seychelles	NOAA	F	4.7°S	55.2°E	3
SHM	Shemya Isl., Alaska	NOAA	F	52.7°N	174.1°E	40
SIS	Shetland Isl., UK	MPI-BGC	F	59.9°N	1.3°W	46
SSL	Schauinsland	UBA	C	47.9°N	7.9°E	1205
SMO	Tutuila, American Samoa	AGAGE	C	14.3°S	170.6°W	42
SPO	South Pole, Antarctica	NOAA	F	89.98°S	24.8°W	2810
STM	ocean stn. M, Norway	NOAA	F	66.0°N	2.0°E	7
SUM	Summit, Greenland	NOAA	F	72.6°N	38.5°W	3238

4

1 Table 4. continued

2

ID	Station	Network	Type	Latitude	Longitude	Altitude (masl)
SYO	Syowa Stn., Antarctica	NOAA	F	69.0°S	39.6°E	11
TAP	Tae-ahn Peninsula, Taiwan	NOAA	F	36.7°N	126.1°E	20
TDF	Tierra del Fuego, Argentina	NOAA	F	54.9°S	68.5°W	20
THD	Trinidad Head, California	AGAGE	C	41.1°N	124.2°W	107
TTA	Griffin, UK	UEDIN	C	56.6°N	3.0°W	535
UTA	Wendover, Utah	NOAA	F	39.9°N	113.7°W	132
UUM	Ulaan Uul, Mongolia	NOAA	F	44.5°N	111.1°E	914
WIS	Negev Desert, Israel	NOAA	F	31.1°N	34.9°E	400
WKT	Moody, Texas	NOAA	F	31.3°N	97.3°W	708
WLG	Mt. Waliguan, China	NOAA	F	36.3°N	100.9°E	3810
ZEP	Ny-Alesund	NOAA	F	78.9°N	11.88°E	475
ZOT	Zotto, Russia	MPI-BGC	F	60.8°N	89.4°E	415

3
4 Table 5. A priori and a posteriori calibration offsets (ppb) relative to the NOAA2006A scale.
5 Note that only LMDZ4-I and TM5-I included the optimization of calibration offsets and only
6 TM5 calculated these annually (the range over all years is given in brackets for TM5-I).

7

ID	Prior	TM5-I	LMDZ4-I	ID	Prior	TM5-I	LMDZ4-I
BIK	0.06	0.22 (0.00 – 0.47)	0.13	PAL	0.50	0.00 (0.0 – 0.0)	0.32
CBW	0.27	0.52 (0.25 – 0.76)	0.84	MHD	0.25	0.08 (0.25 – 0.76)	0.05
HUN	1.08	0.45 (0.24 – 0.59)	0.44	THD	-0.30	0.04 (-0.01 – 0.07)	0.28
LUT	-3.0	-1.2 (-2.0 – 0.0)	-2.0	RPB	0.00	-0.11 (-0.21 – 0.0)	0.07
OXK	0.39	0.77 (0.0 – 1.28)	1.13	SMO	0.20	0.24 (0.14 – 0.37)	0.36
TTA	0.00	0.56 (0.0 – 1.03)	0.65	CGO	0.20	0.08 (0.0 – 0.13)	0.00
JFJ	0.00	-0.47 (-0.69 – 0.34)	-0.60	NIES	-0.60	0.00 (0.0 – 0.0)	-0.41
SSL	0.00	0.30 (0.07 – 0.50)	0.17	MPI-BGC	0.00	0.38 (0.19 – 0.54)	0.47

8
9 Table 6. Overview of the prior and posterior global annual total source (upper panel) and sink
10 (lower panel) (both in TgN yr⁻¹).

11

Year	Prior	MOZART4-I	ACTMt42l67-I	TM5-I	TM3-I	LMDZ4-I
2006	16.3	14.1	16.0	16.9	15.1	17.6
2007	16.8	15.6	16.7	16.9	16.6	19.1
2008	16.2	15.7	16.5	17.2	16.4	19.4
2009	16.4	14.4	15.5	15.4	15.6	18.8
2006	-	12.8	11.9	12.2	12.4	12.7
2007	-	12.6	12.4	12.6	12.4	12.7
2008	-	12.6	12.5	12.4	12.5	12.5
2009	-	12.7	13.0	12.4	12.6	12.7

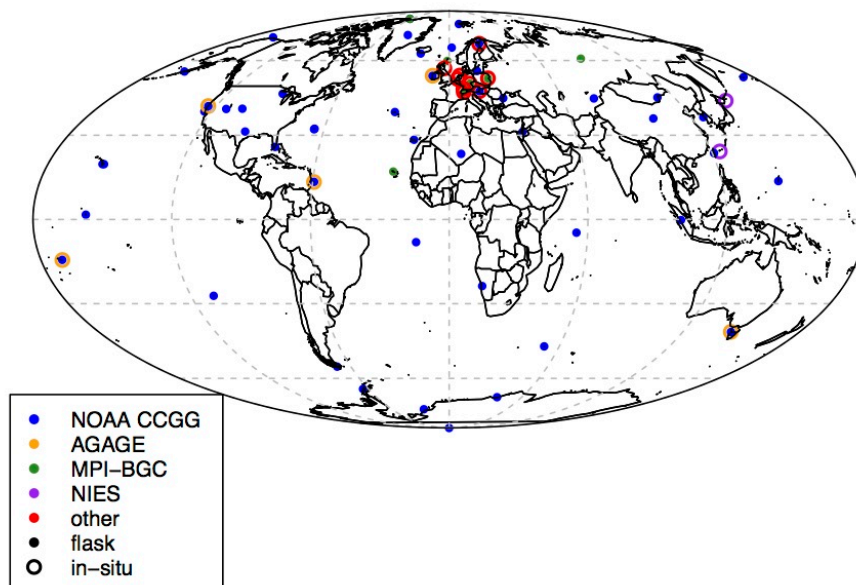
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1 Table 7. Annual mean (2006 – 2008) regional N₂O emission estimates (TgN yr⁻¹). Values for
 2 which the inversions differ on the direction of the change with respect to the prior are shown
 3 in brackets. (MAD = Median Absolute Deviation).
 4

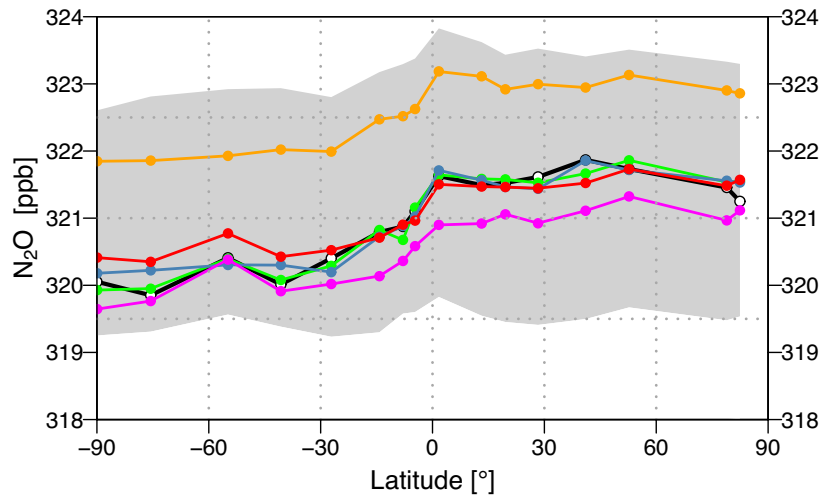
Region	Prior	Posterior		MAD	LMDZ4-I uncertainty
		Range	Median		
ocean 90°S-30°S	1.49	0.92 – 1.34	1.08	0.20	0.39
ocean 30°S-30°N	3.30	3.25 – 3.69	(3.66)	0.03	0.61
ocean 30°N-90°N	0.95	1.13 – 1.29	1.20	0.08	0.32
S + Tr America	2.55	1.99 – 2.62	(2.33)	0.27	1.13
N America	1.00	0.65 – 1.29	(0.74)	0.11	0.28
Africa	3.07	3.23 – 3.40	3.36	0.04	0.70
Europe	0.80	0.84 – 1.20	1.04	0.20	0.19
N Asia	0.40	0.31 – 0.67	(0.40)	0.09	0.42
S Asia	2.91	2.56 – 3.81	(2.85)	0.28	0.77
Australasia	0.39	0.27 – 0.36	0.31	0.01	0.23

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 6

1 Figure 1. Map of surface sites for atmospheric N₂O observations.
2
3

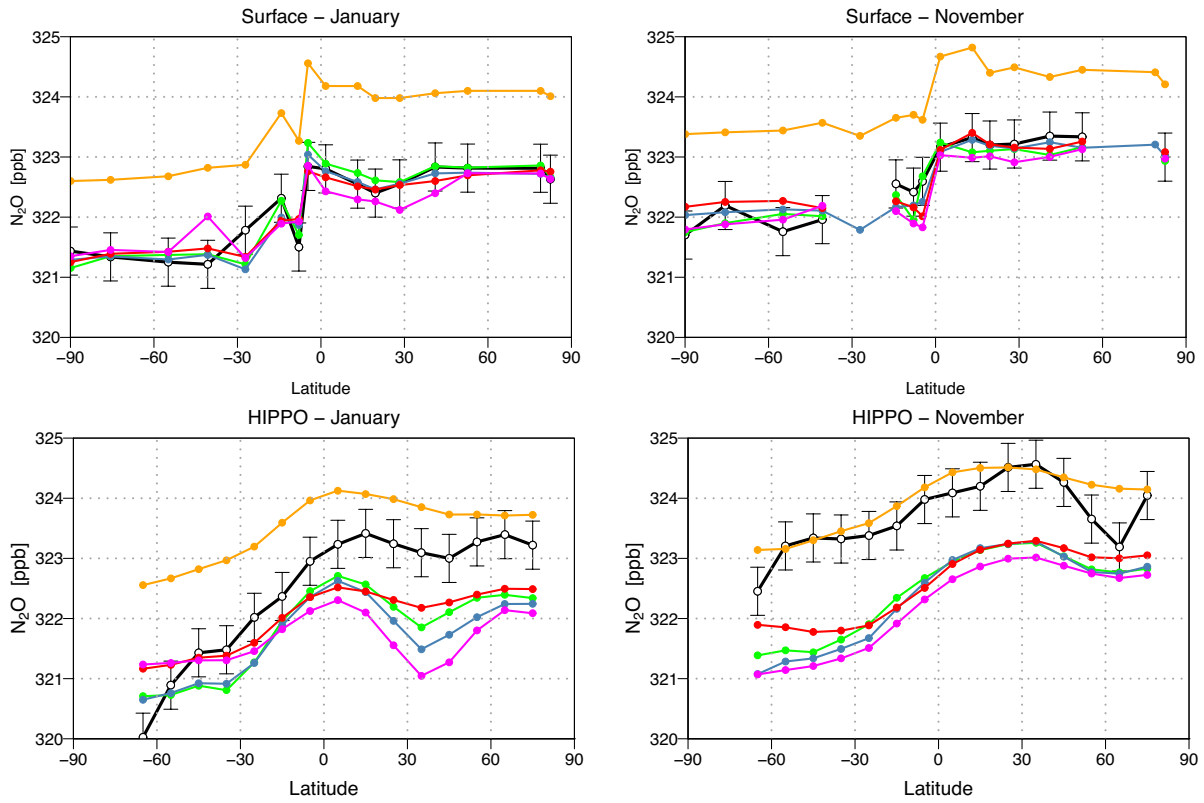


1 Figure 2. Comparison of the annual mean meridional N₂O mole fraction (ppb) from the
2 posterior simulations with that from surface observations (average 2006 – 2009). The grey
3 shaded area shows the range of values for all models using the prior fluxes. (Legend:
4 observations, black; MOZART4-I, orange; ACTMt42l67-I, green; TM5-I, blue; TM3-I, red;
5 LMDZ4-I, magenta).
6



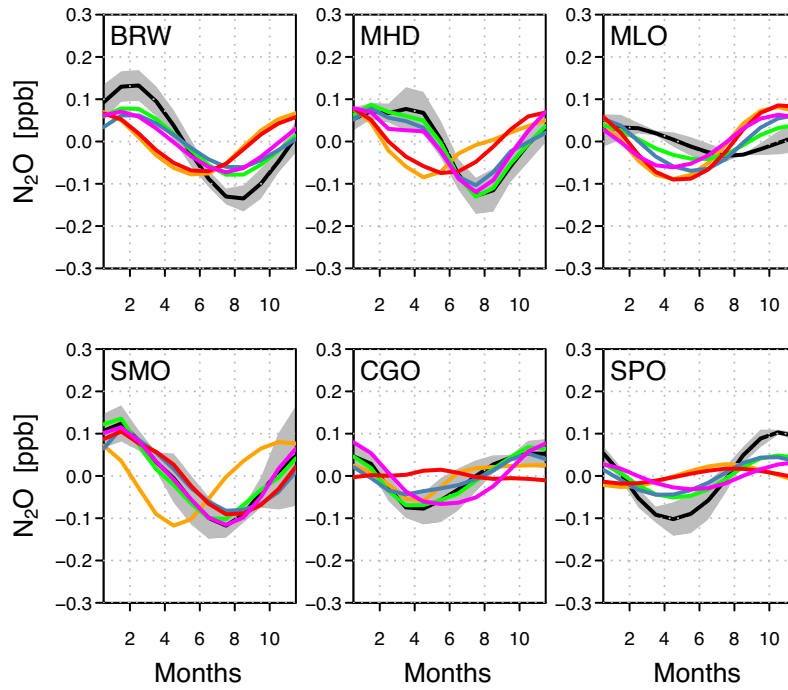
1 Figure 3. Comparison of model simulations (using the posterior fluxes) with observations of
 2 N₂O mole fraction (ppb) from surface sites (top row) and pressure-weighted column averages
 3 (up to 10000 m) from HIPPO aircraft profiles (bottom row) for January (left) and November
 4 (right) 2009. (Legend: observations, black; MOZART4-I, orange; ACTMt42167-I, green;
 5 TM5-I, blue; TM3-I, red; LMDZ4-I, magenta).

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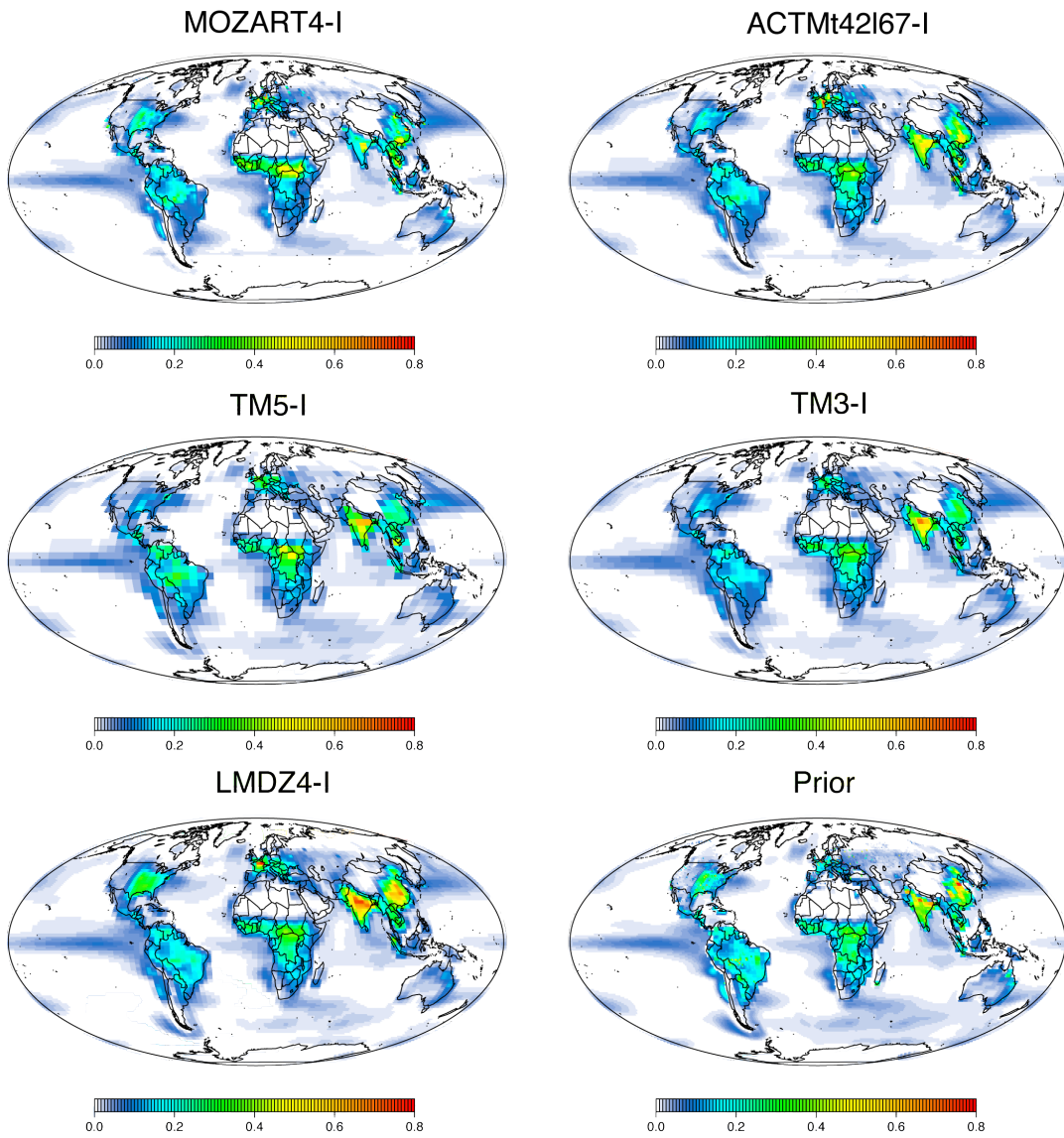
1 Figure 4. Comparison of the mean (2006 – 2008) observed and simulated seasonal cycles
2 (using the posterior fluxes) in N₂O mole fraction (ppb) at selected key sites. The grey shaded
3 indicates the range of uncertainty (1 σ standard deviation) in the observations. For a
4 description of the site abbreviations see Table 4. (Legend: observations, black; MOZART4-I,
5 orange; ACTMt42167-I, green; TM5-I, blue; TM3-I, red; LMDZ4-I, magenta).

6
7

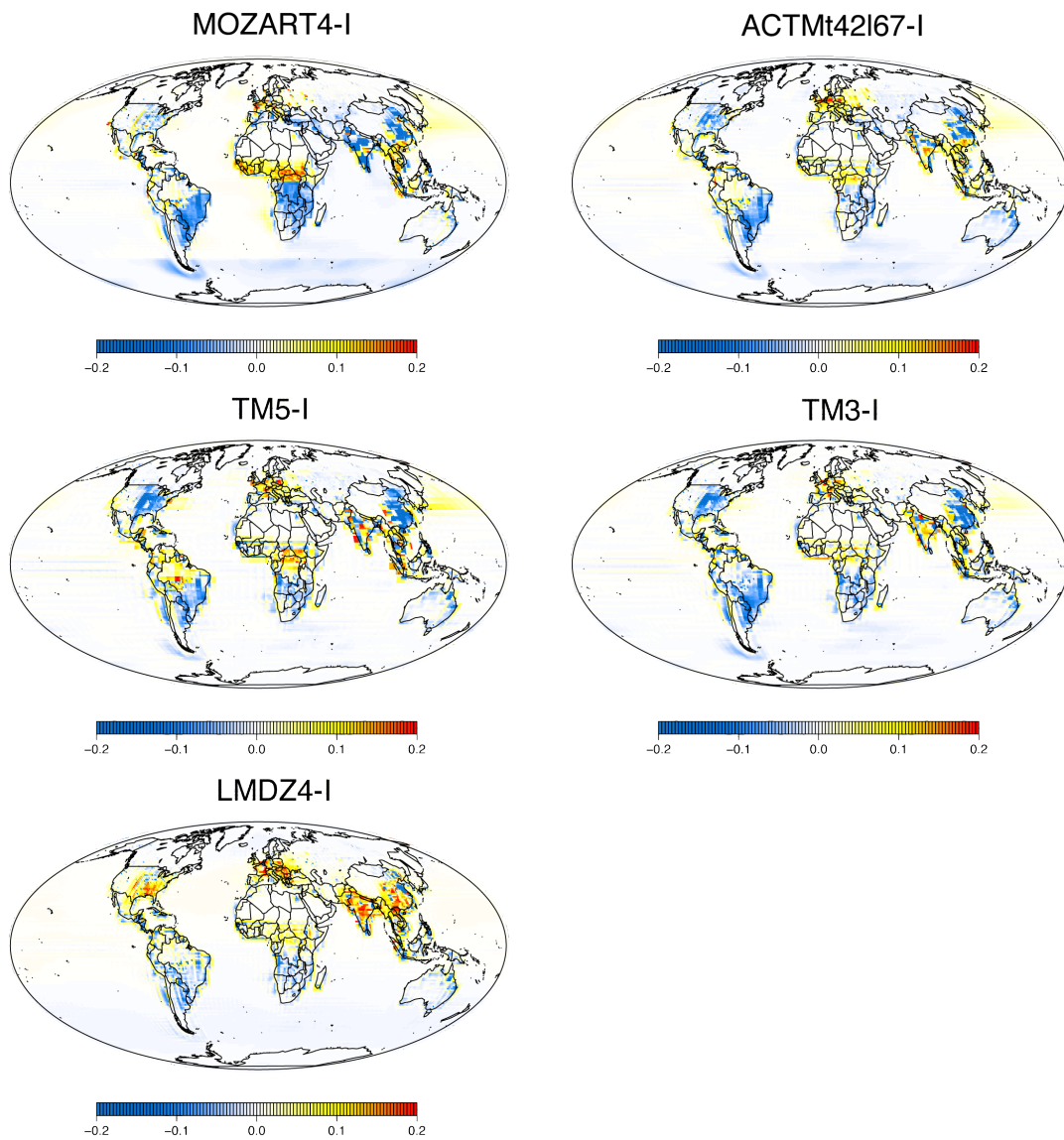


1 Figure 5. Maps of annual mean posterior and prior N₂O flux (gN m⁻² y⁻¹) for 2006 – 2008.

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4



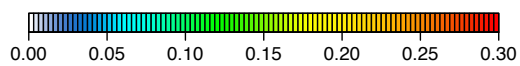
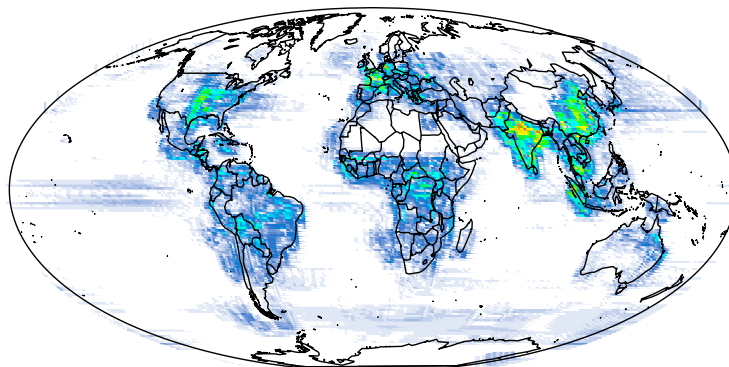
1 Figure 6. Maps of annual mean flux increments for 2006 – 2008 ($\text{gN m}^{-2} \text{y}^{-1}$). Negative values
2 (blue) indicate posterior fluxes that are lower than the prior fluxes and vice-versa for positive
3 ones (yellow - red).
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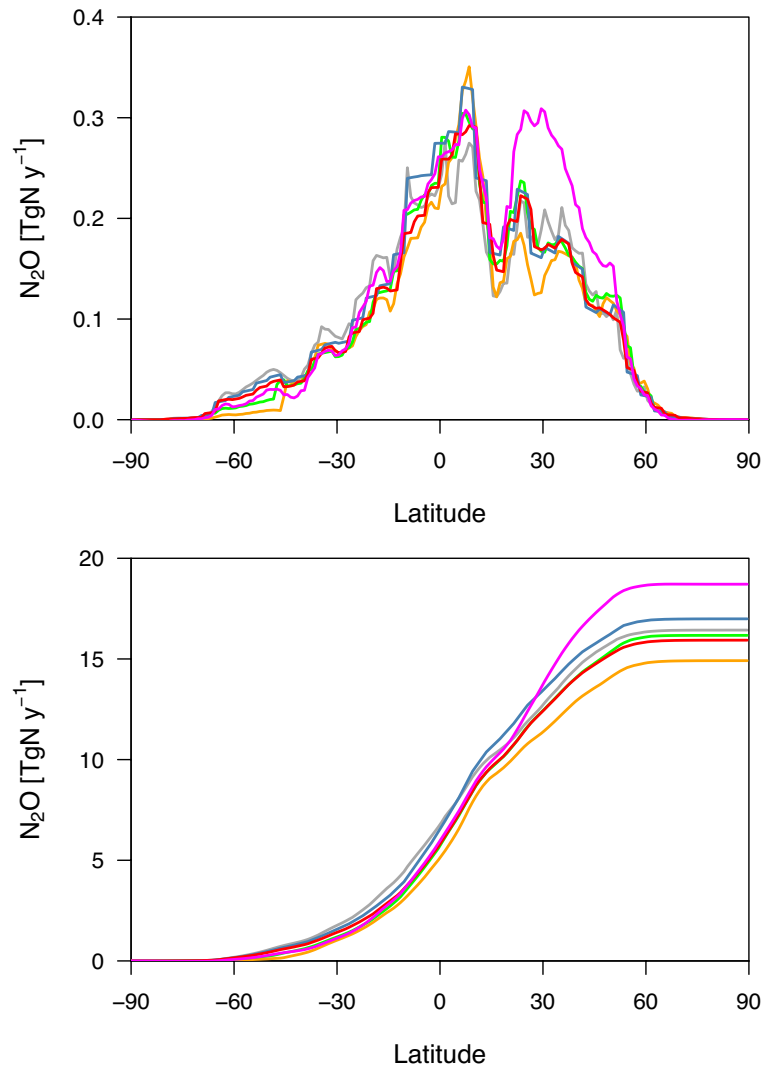
1 Figure 7. Map of median absolute deviation (MAD) of annual mean fluxes ($\text{gN m}^{-2} \text{y}^{-1}$). The
2 colour scale from white to red shows indicates increasing MAD values.

3
4

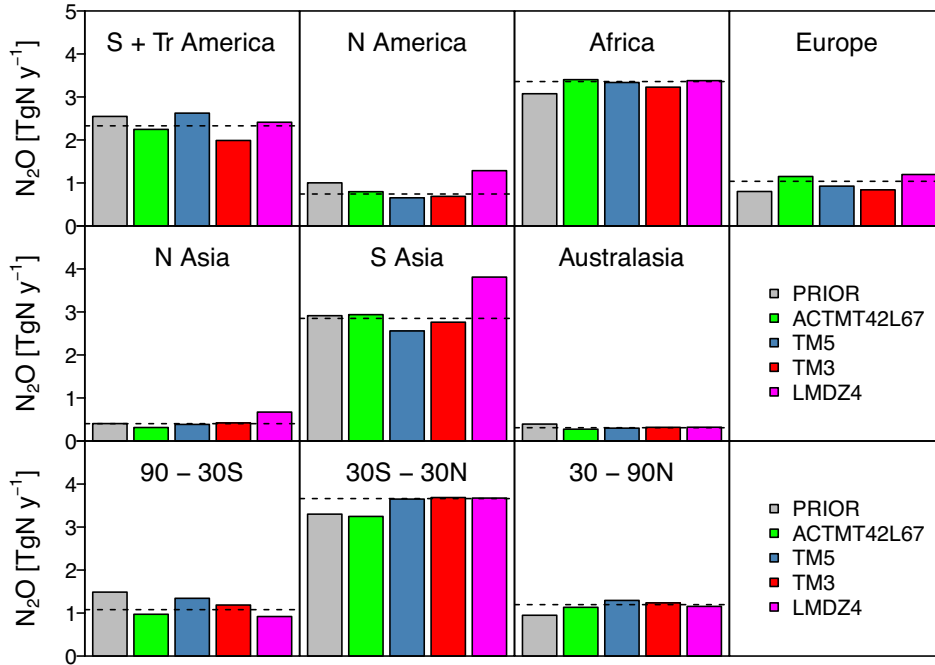


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1 Figure 8. Zonally integrated annual mean (2006 – 2008) fluxes (top) and accumulated from
2 south to north (bottom). (Legend: prior, grey; MOZART4-I, orange; ACTMt42167-I, green;
3 TM5-I, blue; TM3-I, red; LMDZ4-I, magenta).
4
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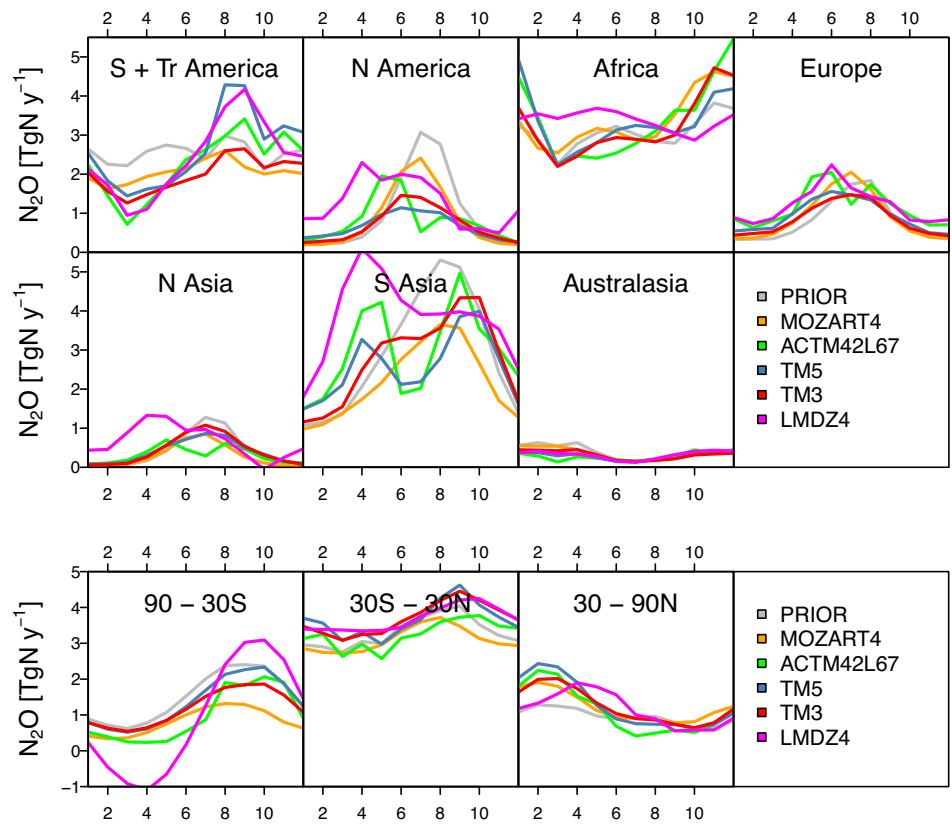


1 Figure 9. Annual mean (2006 – 2008) regional emission estimates (TgN yr^{-1}) for the 7 land
 2 regions (first 2 rows) and 3 ocean regions (last row). The colours refer to the different
 3 inversion frameworks as indicated in the legend and the dashed line is the median of the
 4 posterior emissions.



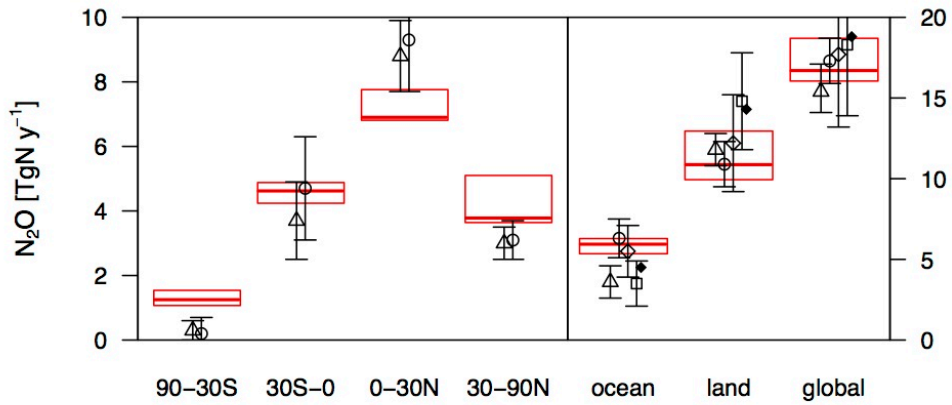
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1 Figure 10. Mean (2006 - 2008) seasonal cycle in N₂O flux (TgN yr⁻¹) for each of the 7 sub-
 2 continental regions (first 2 rows) and 3 ocean regions (last row).
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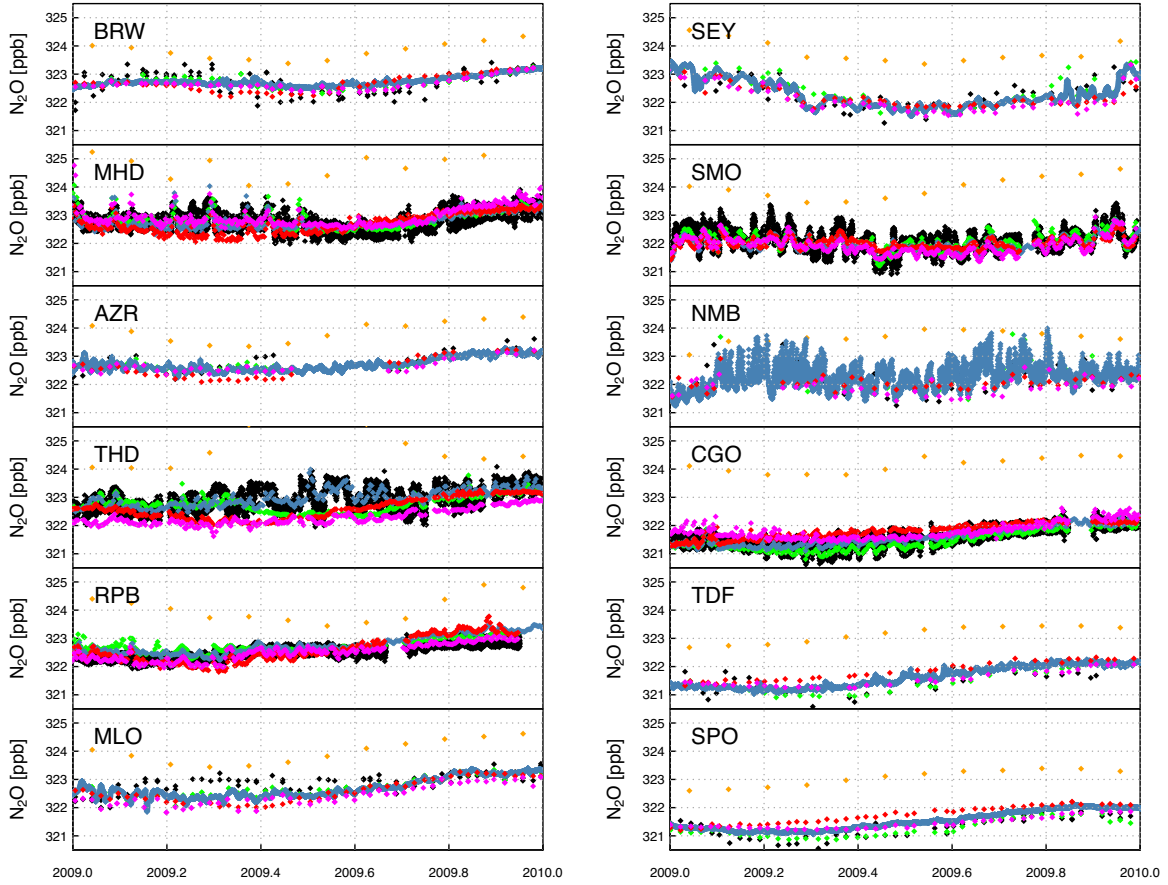
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1 Figure 11. Comparison of the total emissions for each semi-hemisphere region, the ocean,
 2 land and globally from this study with previous estimates. The vertical extents of the red
 3 boxes indicate the range and the horizontal lines in the interior indicate the median of
 4 inversion estimates from this study. The points indicate the values from previous studies:
 5 Hirsch et al. (2006), open circles; Huang et al. (2008), triangles; AR4, diamonds;
 6 Syakila et al. (2011), solid circles; Zaehle et al. (2011), squares. The error bars indicate the 1σ
 7 uncertainty.
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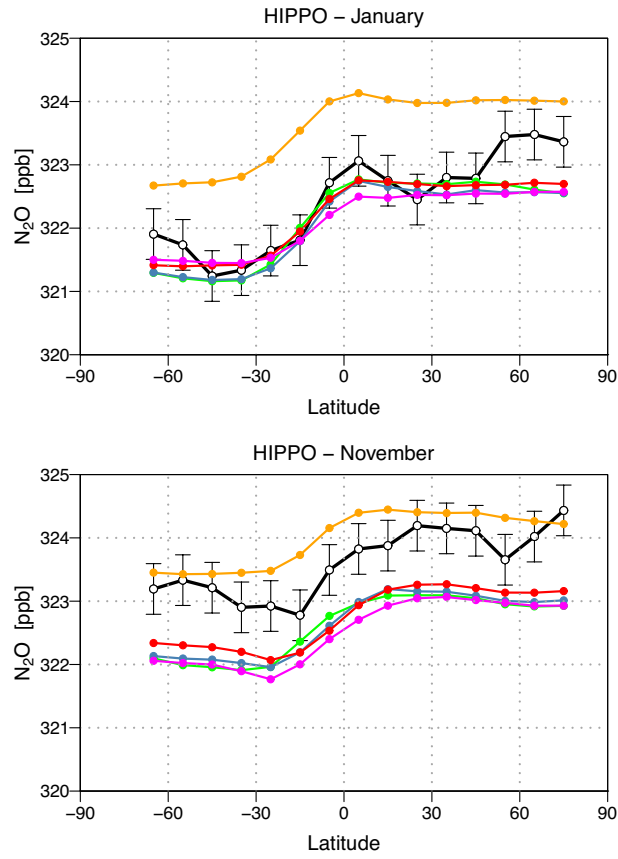
1 Figure S1. Comparison of the daily mean N₂O mole fractions (ppb) for 2009 simulated by
2 integrating the CTMs with their corresponding posterior fluxes. Note for MOZART4-I only
3 monthly means were submitted. (Legend: observations, black; MOZART4-I, orange;
4 ACTMt42l67-I, green; TM5-I, blue; TM3-I, red; LMDZ4-I, magenta).

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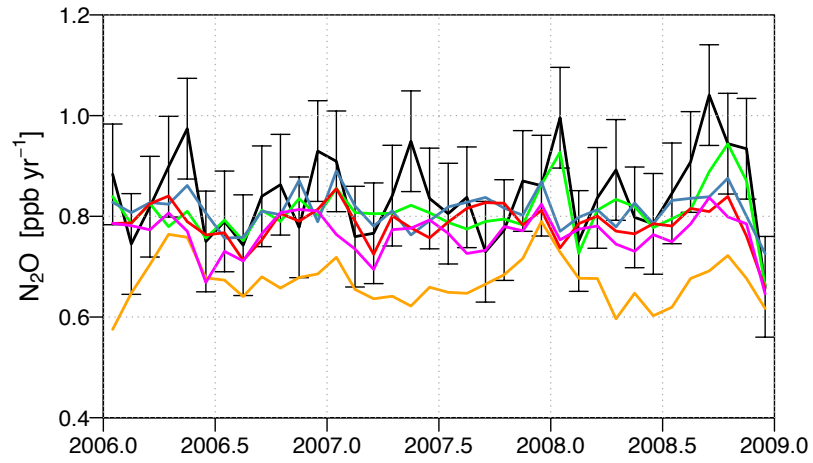


1 Figure S2. Comparison of model simulations with pressure-weighted column averages from
2 HIPPO aircraft profiles for January (top) and November (bottom) 2009. The column average
3 was calculated from the surface up to 2000 m. (Legend: observations, black; MOZART4-I,
4 orange; ACTMt42167-I, green; TM5-I, blue; TM3-I, red; LMDZ4-I, magenta).

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- 1 Figure S3. Growth rate in atmospheric N₂O mole fraction (ppb yr⁻¹) for 2006 to 2009.
- 2 (Legend: observations, black; MOZART4-I, orange; ACTMt42167-I, green; TM5-I, blue;
- 3 TM3-I, red; LMDZ4-I, magenta).
- 4



- 1 Figure S4. Map of the 7 sub-continental regions used in the analysis. (North America = green,
- 2 Tropical & South America = red, Africa = yellow, Europe = cyan, North Asia = blue, South
- 3 Asia = purple, Australasia = magenta).
- 4

