Reply to: Interactive comment on “Inverse modelling of European N_2O emissions: assimilating observations from different networks” by M. Corazza et al.

Anonymous Referee #1
Received and published: 5 November 2010

General Comments:

1. *It seems hard to believe that the model calculates the same fluxes and biases among different networks regardless of whether the NOAA measurements, which are considered as the universal standard, are included. I am comfortable with the idea that the inversion can simultaneously solve for biases and optimal fluxes if the NOAA data are included, but I don't understand how this can be true without them, given that a bias is calculated for each individual station (rather than network) and that the fluxes have a heterogeneous spatial distribution and vary over a factor of 10 in magnitude (Figure 3). Could the model primarily be balancing out the atmospheric N2O values at different sites to bring them all to a relatively uniform value? Judging from Figure 2, this seems to be the case, with all stations showing an posteriori value around 320.5 ppb. What kind of spatial gradients then are left in the data to help guide the estimate of the spatial distribution of sources? To help answer these questions, it might be useful to show in the Supplementary Figures a contour map, for a selected month or two, of the observed atmospheric N2O mixing ratio over Europe before and after the bias corrections.*
   Regarding the use of the NOAA flask data as the unbiased standard, I am concerned about using bi-weekly flask data, with an average flask pair agreement of 0.4 ppb, to identify biases in the in situ data. It is considerably easier to filter out anomalous readings and problems associated with data representativity using high frequency in situ data rather than flask data, especially for a gas with low signal to noise like N2O. What kind of biases might be introduced in the inversion due to uncertainties in the NOAA data?

   The fact the S4 results in very similar bias corrections (and a posteriori emissions) as S1 demonstrates that the monitoring stations are strongly linked via atmospheric transport, especially during synoptic situations with higher wind speeds (when emissions have a smaller impact on the mixing ratios, and the mixing ratios are close to the 'baselines' of the stations). During the inversion period (14 months) many different synoptic situations are encountered (e.g. situations where air masses are transported from station A to B, but also from B to A), which apparently allow the inversion system to differentiate between differences of mixing ratios (station B - station A) arising from emissions between the stations (which depend on the wind direction) from differences arising from the calibration offset (which is independent from the wind direction / synoptic situation).

The use of bias correction implies that the inversion system cannot derive any information from the spatial gradient between the stations (for those stations which have independent bias corrections), but utilize the information within the footprint of each station independently, while the bias correction allows to make the measurements (especially their baselines) consistent with each other.

Regarding the use of the NOAA flask data as unbiased reference: most important is that the NOAA flask samples are centrally analyzed in one single laboratory. This should minimize the risk of systematic biases between different sites (although some biases in time cannot entirely be excluded).
Assuming that the precision of 0.3-0.4 ppb for the NOAA samples (single measurement) largely reflects random errors, these measurements should provide a good reference, when analyzing annual mean biases, since the uncertainty for the mean bias should scale with 1/sqrt(n) (e.g. for 26 samples per year (bi-weekly sampling): 0.3 ppb / sqrt(26) ≈ 0.06 ppb).
We are not including a contour map of the observed atmospheric N2O mixing ratio over Europe before and after the bias corrections, mainly because of the large temporal variability at most stations (mostly arising from local to regional sources). To create such contour maps in a meaningful way would require filtering out signals from such local / regional sources to visualize mean gradients of the background values at the different stations.

We agree that using high frequency data is useful to filter out anomalous readings and problems associated with data representativity. However, in presence of biases, the availability of high frequency data does not help, since any systematic deviation is expected to affect all available data, independently on their frequency, and can be corrected only relying on a reference that can be considered unbiased.

2. *Re: Section 4.2.2: It seems somewhat misleading to say the model improves a priori emissions if the main improvement is to scale up emissions. Simple back of the envelope calculations, such as those described in Hirsch et al. [2006], make it clear that the GEIA inventory at 13.6 TgN/yr substantially underestimates total N2O emissions. A more challenging question is whether the 4DVAR method can improve the spatial and temporal distribution of emissions. It would be interesting to tabulate whether the relative percentage of European emissions on a country-by-country is changed significantly for prior and posterior fluxes. Clearly Britain's relative share must decrease, based on Figure 3, but I see no obvious reason why Britain's emissions should be overestimated by either GEIA (Figure 3) or the UNFCC (Figure 5) while most of the rest of Europe has been underestimated. This seems more likely to be an artefact of the inversion rather than a real result.*
   On a related note, please give a reference and brief description of the UNFCC estimates. These are reported, I believe, on a country-by-country basis and are estimated using a different methodology than the gridded GEIA sources used as the prior.

Following the reviewer's suggestion, we included in the manuscript a statement that our a priori inventory obtained from different sources (GEIA, GFED v2, EDGAR 4.0) likely underestimates the annual totals (page 26329). Accordingly, we also modified the text in the results in order to make it clear that we expected the system to scale up total annual emissions over the global domain (page 26336). Furthermore, we added a new table, compiling the country totals. At this point it remains rather speculative, whether the negative inversion increment for UK and Ireland compared to positive increments for most of the central continental European countries are due to systematic errors in the bottom-up inventories or due to systematic errors in the inversion. We emphasize again, however, that the inversion increments are in general relatively small (in particular in view of the very large uncertainties of the bottom-up inventories).

We added a reference for the UNFCCC data at page 26339.

3. *The seasonal cycle in N2O data over Europe has an amplitude around 0.7 ppb, with a relatively deep minimum in late summer, which is probably caused in large part by an influx of depleted air from the stratosphere. Given that the inversion is restricted to a 1 year time span, how can we be sure that the inversion is properly partitioning seasonality in the data between surface sources and stratospheric influences? Could the stratospheric influence be affecting the seasonality of sources presented in Figure 5? Some additional, related comments: a) p.26329 states that the stratospheric destruction reactions have pronounced seasonality, but the more relevant issue is the seasonality of Strat-Trop Exchange. Do we have evidence that the TM5 captures the seasonality of STE accurately? b) Please describe in more detail how high the TM5 model extends into the stratosphere and how the ECHAM5/MESSy1 sinks are incorporated into the TM5. c) Is there a reference to support the claim that the May-June emissions peak in Figure 5 is "very likely" (p.26340, line 15) related to fertilizer use in Europe? (It seems perhaps a bit late for a spring fertilizer application.) Also, why would Benelux or Britain have a fall emissions peak, in contrast to many of their neighbors, given that these countries have N-intensive agricultural production? An acknowledgement that some if not most of the apparent seasonality in the fluxes may arise from uncertainties in the model, particularly in the handling of STE, might be needed.*

We agree about the importance of the vertical transport and of the tropospheric-stratospheric exchange simulated by the model and about the potential influence that an erroneous treatment of these processes may have on the derived emissions and their seasonality. The STE is a key issue that has been investigated for TM5 in different studies:

- Bregman et al., 2006, http://www.atmos-chem-phys.net/6/4529/2006/acp-6-4529-2006.html.
- de Laat et al., 2007, http://www.agu.org/pubs/crossref/2007/2005JD006789.shtml.
- de Laat et al., 2009, http://www.atmos-chem-phys.net/9/8105/2009/acp-9-8105-2009.html.

First comparisons of the N2O model fields simulated in the study with NOAA aircraft profiles show generally good agreement (results not shown in the paper). However, this issue clearly needs to be further analyzed in subsequent studies. We added in the text a paragraph pointing out the sensitivity of the derived seasonality of emissions on the treatment of the stratospheric-tropospheric exchange (page 26340). Also some modifications to the manuscript related to the comments of the second Referee go in this direction.

a. See discussion above.
b. A description of the top layer described by the model in the stratosphere has been included (page 26328).
c. we agree with the comment of the Referee and we changed "Very likely due" with "that can be associated" in the text. Also, a new paragraph has been added at page 26340.

Minor comments:

Abstract, line 23: The sentence about Southern Europe is ambiguous. Please state more clearly: done.

p.26324, lines 4-5, please give a better quantitative summary of the number of stations. "various" and "a number of" are unnecessarily vague terms: done.

p.26326, line 8. The Dlugokencky et al. [1994] reference is for methane and predates the start of the NOAA N2O program by several years. I don't think there is an updated reference specific to the analytical aspects of the N2O flask program, but perhaps a reference like Hirsch et al. [2006] should be added: Hirsh et al. 2006 added as suggested.

p.26325, last full paragraph. Please clarify which stations have in situ data, etc. It is ambiguous as written whether the stations other than the CHIOTTO towers are in situ: all continuous measurements (as compiled in Table 1) are in situ measurements.

p.26330, line 1, sentence beginning, "Due to the correspondence…" Please clarify this confusing sentence: the sentence has been modified.

p.26331, While I understand the need for brevity, it would be useful to give a short explanation of what the variables actually are, beyond a purely mathematical description. Some of the less obvious terms are B and H. What is the "background error" and what goes into H? Is it, e.g, an adjoint of the TM5?: "background" has been substituted by "a priori state vector". The sentence for the description of H has been modified. The characteristics of **B** are discussed at the end of the paragraph, those of **R** in section 3.3.

p.26334, lines 1-2 and throughout paper. "Associated to" should be "associated with": done.

p.26336, line 3, "Shortly" should be "briefly": done.

Figure 1, please clarify in the caption whether the biases to the right of the plots are those estimated in the inversion or calculated directly from the data comparison: caption modified according to referee' suggestion.

Figure 2 needs x-axis label, at least at the bottom of the graph: x axis added (Time [days]).

Figure 4. Please explain in more detail why this ratio represents the reduction of uncertainty: Added an explanation of the ratio.

References

Bregman, B., Meijer, E., and Scheele, R.(2006), Key aspects of stratospheric tracer modeling using assimilated winds, Atmos. Chem. Phys., 6, 4529-4543, doi:10.5194/acp-6-4529-2006.

de Laat, A. T. J., J. Landgraf, I. Aben, O. Hasekamp, and B. Bregman (2007), Validation of Global Ozone Monitoring Experiment ozone profiles and evaluation of stratospheric transport in a global chemistry transport model, *J. Geophys. Res.*, 112, D05301, doi:10.1029/2005JD006789.

de Laat, A. T. J., van der A, R. J., and van Weele, M. (2009), Evaluation of tropospheric ozone columns derived from assimilated GOME ozone profile observations, Atmos. Chem. Phys., 9, 8105-8120, doi:10.5194/acp-9-8105-2009.