Review of 'Limitations of ozone data assimilation with adjustment of NOx emissions: mixed effects on NO2 forecast over Beijing and surroundings areas'

The manuscript of Tang et al. elucidates potentials and limits of the Ensemble Kalman filter (EnKF) for chemical data assimilation (DA) and cross-correction of reactive gases and emissions (O3 and NOx) in the framework of air-quality forecasts. The first part of the paper provides an extended validation of the previous study of Tang et al. (2011) with a focus on NO2 forecasts. The observed degradation of NO2 forecasts at some locations motivates the authors to examine the behavior of EnKF in a simplified model setting. DA experiments in such a controlled environment permit to identify the likely cause of the degradation, i.e. strong non-linearities between the controlled NOx emissions and the observed/assimilated O3 concentration.

First, I appreciated the fact that the authors further validated their previous study and published these new results, even if this partially question the method that was employed in Tang et al. (2011). The EnKF is a powerful and flexible DA algorithm but requires particular care when applied to correct unobserved variables or parameters in complex models. Studies that use EnKF to cross-correct unobserved variables or model parameters should more often try to provide in-depth validation of assimilation results, as the authors did here.

Second, I liked the methodology that was used by the authors, i.e. reproduce the observed behavior within a simplified model. This allowed a reasonable scientific explanation for the NO2 degradation and, more in general, permitted to highlight the effect of strong non-linearities in chemical DA. As the authors also stated, this topic is often not well discussed in the chemistry DA literature and deserves further research. It would have been nicer if the authors could propose an algorithm to automatically detect strong non-linear regimes and at least avoid the analysis degradation within the EnKF. This limits a bit the impact of the study for the air-quality DA community.

The manuscript is concise and well structured, although multiple sentences should be rewritten in a better English. Hence, I recommend publication in ACP as a companion paper of Tang et al. (2011), after the following comments are considered.

Specific comments:

1) Page 35694, line 27: *'the fast variability of the relationship between ozone concentrations and NOx emissions*' is not very clear. The O3-NOx emissions 'relationship' is a result of complex chemical reactions involving other species, radiation, temperature etc.. Therefore, the 'relationship' is by definition not unique and saying that it varies 'fast' has not a precise scientific meaning. I suggest the authors to either remove this sentence or rephrase to make it scientifically sound.

2) Page 35695, line 14-15: '*... the divergence of the influences of the initial condition optimization ...*' is not clear. Do the authors mean that the initial condition has a weak influence on chemical forecasts? Please rephrase. It is also worth reminding that chemical species have a large range of life-times and can

depend on different processes (emissions, photolysis etc.). This implies that this statement is not very informative without saying to which species and which forecast's duration we refer to.

3) Page 35695, line 24: I could not find demonstrations of improvements of ozone forecasts in Hanea et al (2004). Please remove the reference if not pertinent to the text.

4) Page 35698, line 8-9: *'fully supports nonlinear evolution of a model...*' might lead to a wrong interpretation since the EnKF is based on gaussian hypothesis and, as the authors show, it fails when non-linearities become too prominent. I guess the authors mean that EnKF can be implemented quite easily because the full non-linear model is employed during the ensemble forecast step. Please rephrase.

5) Page 35698, line 16: see comment 3 for Hanea et al. 2004, Lin et al. 2008 is missing in the list of references and van Loom et al. 2000 does not demonstrate improved forecast skills for ozone (this concerns also page 35709, line 1). I suggest the authors to provide a more complete list of references that demonstrate the successful improvement of reactive gases forecasts through DA. Otherwise the authors should acknowledge that more research is needed in this regard.

6) Page 35699, line 9-10: are the samples extracted from a normal distribution? Can the authors also precise the criteria that have been used to choose an ensemble of 50 members. How were the assimilation performances evaluated?

7) Page 35701, Sec. Data assimilation algorithm: Are the authors using some inflation and/or localization technique for the EnKF? If yes please describe it briefly in the text.

8) Page 35702, Sec. Surface observation network: the authors should report some information about the measurement method and instrumental uncertainties of the employed in-situ NO2 measurements. The issue of representativity of NO2 measurements for the model grid should also be briefly discussed. Compared to O3, NO2 measurements in urban environment can be largely affected by local pollution and be not representative of a 10km model pixel. For example, are some of the used NO2 sites exposed to heavy road traffic?

9) Page 35703, lines 10-13: It is not very clear to me why small emissions of NOx cannot undergo *'significant'* changes with DA. If the variance of the ensemble is set as a percentage of the NOx emissions themselves, the DA correction is expected to be also proportional to the emissions and, therefore, locally significant. This should be the case unless the O3 is not sensitive to NOx in low NOx regimes. Can

the authors provide more insights on this? Looking at the corresponding O3 ensemble spread and EnKF correction at suburban sites could also help.

10) Page 35704, lines 23-24: larger errors of modeled NO2 in ppb units can also just be related to larger values of NO2 concentration, which normally occurs in early morning and late evening, when NO2 photo dissociation is not active and the boundary layer is shallow. Is the percentage error showing the same behavior?

11) Page 35708, lines 6-7: ' ... *except for dealing with the non-linear relationship* ...'. this part of the sentence is not clear, please clarify what you mean by 'except' and rephrase in case

12) Page 35708, line 23: *'rapid variations'* see comment n. 1

13) Page 35709, lines 17-20: The largest non-linearities arise from the chemical mechanism. Please explain why changing the model resolution would affect the non-linear behavior of the system and therefore the results of DA.

14) Page 35709, lines 19-20: *'Except for inversely estimating emissions* ... ' I cannot understand the exception. Doesn't this study show that the estimation of NOx emissions assimilating O3 observation deals with chemical non-linearities? Please clarify this sentence.

Technical corrections:

Please consider proof-reading the manuscript by an English native speaker. I provide here some suggestions for some sentences that should be ameliorated.

1) Page 35694, lines 2-3 '... *that has been validated as an efficient approach for improving ozone forecast*' -> ' that has been used in the companion study to improve ozone forecasts over Bejing and surrounding areas'

2) page 35694, line 16: remove *'as a further investigation'*

3) page 35695, line 7: '... *that closely integrates ... is recognized* ... ' > ' ... integrates ... and is recognized ...'

4) page 35700, lines 8-9: remove *'provide various ... initial estimations) and* '

5) page 35704, line 8: ' *varies from the day to the night and the morning*' > ' is different between day-time, night-time and morning hours'

6) page 35706, lines 11-13: '... *are combined by EnKF to produce linear correlations between them during the calculation of* ...' does not sound very well in English, please rephrase

7) page 35706, lines 24-28: same as above

Tang, X., Zhu, J., Wang, Z. F., & Gbaguidi, A. (2011). Improvement of ozone forecast over Beijing based on ensemble Kalman filter with simultaneous adjustment of initial conditions and emissions. Atmospheric Chemistry and Physics, 11(24), 12901–12916. doi:10.5194/acp-11-12901-2011