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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Accounting for non-linear chemistry of ship plumes in the GEOS-Chem global chemistry transport model" *by* G. C. M. Vinken et al.

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We thank you for the review and constructive comments provided. Please find our detailed replies to your comments below. We adapted our manuscript in line with your recommendations. We marked updates in our manuscript corresponding with this review with a blue text color.

General comments

1) It is correct that the paper offers a comprehensive description of the method how the chemical non-linearities in the diluting plume are taken into account, but in my opinion very few space is given to the discussion of its limitation. The 'fraction of NO_x *remain-*

ing' and integrated NOPE are in fact a function of the environmental conditions neither at the initial release time, nor at the actual emission into CTM (5h later), but of their entire evolution during the dilution. Although authors assume that these parameters do not change 'dramatically' during the plume dilution, the reality can be very different (e.g. photolysis rates can drop significantly when moving below a cloudy area during the first 5 hours after the injection). How would the model results be affected - improved, if some integrated (averaged) environmental parameters were accounted for, i.e. the global CTM 'remembered' the environmental conditions from the last 5 hours of integrations?

It is true that environmental conditions for a ship plume can change during plume evolution, and we do take such changes partly into account ($\frac{J(\mathrm{NO_2})}{\mathrm{J(O(^1D))}}$ and $J(\mathrm{NO_2})$ follow changes in the solar zenith angle during the 5-hour evolution). However, we propose here a parameterization for general ship plume chemistry in an off-line chemistry transport model (and not a single plume for 'real weather' conditions), and thus cannot account for all changeable conditions. Our chemistry transport model uses off-line GEOS-5 meteorological fields that are updated every 6 hours. As a consequence, the model meteorological state represents a smoothed, 6-hour, grid cell averaged condition for an ensemble of plumes. We argue that this is for the better, since our parameterization aims to describe general plume chemistry occurring for the average of an ensemble of many ship plumes occurring under similar circumstances.

Nevertheless, we agree that rapidly changing meteorological parameters could introduce errors in our calculation of the fraction of $\mathrm{NO_x}$ remaining and the net ozone production efficiency. We estimated these errors by performing a number of additional simulations with PARANOX. Comparing a 5-hour clear sky simulation to one with an overcast situation between t = 1 till 4 hours leads to 5% increase in the fraction of $\mathrm{NO_x}$ remaining and decrease in the integrated net ozone production efficiency. A decrease in temperature by 10 K during the last 2 hours, leads to decreases smaller than 2%. Reducing $\mathrm{NO_x}$ concentrations for the first 3 hours of plume dispersion by 20% results in a 2% increase in the fraction of NO_x remaining, and a 5% increase in the integrated NOPE. We conclude that our assumption of (some) constant environmental parameters during plume dispersion introduces errors in the fraction of NO_x remaining and the integrated NOPE of at most 10%, and that these errors largely cancel when temporal averages are analyzed. Accounting for changing environmental parameters would probably lead to more accurate instantaneous GEOS-Chem simulations, but we think this is currently not feasible because of the large additional memory requirements for the large number of model grid cells with ship emissions (5000+). We now include this error estimate in section 3.3.

2) Although the majority of the abstract concerns the results gained by the new method implemented in GEOS-Chem, the presentation of the actual simulations occupy only two pages in the manuscript. I would suggest to extend this part of the paper by a couple of additional experiments/results: e.g. why the standard model with ship emissions (that replaces 1 NO_x molecule released by 1 HNO_3 and 10 O_3 molecules) was not applied here for comparison of the results (like in the evaluation)? Further, as instant dilution leads to overestimated ozone production and NO_x lifetime, this consequently increases OH concentrations, leading to overestimated CH_4 lifetime decrease. It would be thus interesting to see, how OH is perturbed by the parametrization (and eventually by the introduction of ship emissions themselves, with respect to the non-ship case). What is the vertical extent of the ship NO_x impact as well as the impact of the parameterization itself? - a zonal plot or a longitude cross-section across the Atlantic would be interesting to add. Further I think the results have to be discussed in more details, putting the findings into context using the references from the 'Introduction' and eventually others. The 'Conclusions' further should in my opinion discuss also the future potential improvements of the method considering its limitations (see General comment 1)

We have extended our manuscript and now include a comparison with the standard model in the 'Results' section. It would indeed be interesting to also show the effects on OH and on the vertical distribution of NO_x, but this is beyond the focus of this study on improving the simulation of ship NO_x.

We agree that it would be valuable to discuss our results in the context of literature discussed in the ‘Introduction’ section. However, most of these studies are box model studies, and thus cannot be compared directly to our global CTM simulations. To our knowledge, the paper by Huszar et al. [2010] is the only paper accounting for the non-linear chemistry during ship plume dispersion in a (regional) CTM. In the ‘Conclusions’ section we now discuss the potential improvements and limitations of our method with the following paragraph:

We anticipate that our method could be further improved by increasing the number of dependencies, and the number of entries (to reduce interpolation error) in our look-up table. We expect that taking into account 5-hour integrated environmental parameters (instead of end-of-run) would improve the accuracy of individual instantaneous simulations, but at the expense of significant additional memory requirements. However, with increasing memory of computers this could well become possible.

Specific comments

P17792, L5-8: The reference on Charlton-Perez et al. work is correct but the context why this sentence is included might be not clear. Is it because of the expectation that by increasing resolution, models start to resolve plume processes so, in accordance with the ship plume studies, produce less ozone?

Yes, we included this reference, as this study shows that higher resolution simulations produce less ozone, indicative of the non-linear chemistry that occurs inside the ship plumes. Moreover, this study provides an estimate of the overestimation of the O_3 production.

P17792, L14: Why the authors start the paragraph with “Not a single global CTM currently takes the in-plume effects during ship plume dispersion into account”, if just *a few lines below they refer to GEOS-Chem model in early stages and GMI which actually already account for these processes by not emitting directly NO_x, but O_3 and HNO_3?*

We clarified this sentence in our manuscript.

P17793, L9: Huszar et al. (2010) did not apply the method of effective emission indices but the approach of effective reaction rates (Paoli et al., 2011).

We adapted this in the manuscript.

P17798, L20: Sensitivity analysis: the section already starts with the sensitivity analysis of certain parameters on 'fraction of NO_x remaining' and integrated NOPE, but the reader is left with questions what implications led the authors to choose these parameters and not others. Authors state at P17797, L8 that the sensitivity analysis is performed in order to determine the most critical parameters, but in fact the parameters are already determined before the sensitivity analysis, at least this impression comes to reader.

We have studied several parameters and only present the most important parameters in our manuscript. For clarity, we included a list of all the studied parameters in our manuscript.

P17799, L13-14: Why the authors do not simply examine the dependency on $J(O(^1D))$, as sensitivity test on $J(NO_2)$ is already included?

This is a good point. Indeed, we might as well have simply shown the dependency on $J(\mathrm{O}(^1\mathrm{D}))$. The reason for using the ratio $\frac{J(\mathrm{NO_2})}{\mathrm{J}(\mathrm{O}(^1\mathrm{D}))}$ is merely historical. In an earlier study, we attempted to express the fraction of NO_x remaining and the integrated NOPE as a function of environmental parameters based on an ensemble of GEOS-Chem model simulations using a multiple linear regression. The parameters $\frac{J(\mathrm{NO_2})}{\mathrm{J}(\mathrm{O}(^1\mathrm{D}))}$ is more orthogonal to $J(\mathrm{NO_2})$ than $J(\mathrm{O}(^1\mathrm{D}))$, as by dividing by $J(\mathrm{NO_2})$ we remove the effect of

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clouds on this parameter, i.e. a low value of $\frac{J(NO_2)}{J(O(^1D))}$ is indicative of a high overhead O_3 column, and not of cloud cover. See Vinken [2010] for more details. Please note that using $J(O(^1D))$ or $\frac{J(NO_2)}{J(O(^1D))}$ does not make any difference for our results.

P17799, L15-23: Firstly, I am not sure by the importance of using solar zenith angle θ_0 as parameter to include in the look-up table. Isn't the photolysis rates J(O(^{1}D)) and J(NO$_2$) already contain the relevant information. e.g. at night they equal to zero, at noon they are at maximum (considering clear sky conditions)? Secondly, is the reason to include θ_5 as environmental parameter because we cannot assume about solar zenith angle not to change "dramatically" (P17802, L26)?

The reason to include both θ_0 and θ_5 as parameters is that we use these angles to simulate the variation in the photolysis rates during the 5 hours of expanding. See our response to the first general comment and the next comment.

P17800, L16-21: What are the intervals for the LUT parameters and for how many values from the particular interval was PARANOX run? Was the LUT constructed for every possible combination of these parameters (which could lead to very large number of PARANOX runs; e.g. 10 possible values for each parameter - 10^7 runs, assuming independency between them which of course is not completely true.) Further I assume that environmental parameter (e.g. temperature, background NO$_x$, O$_3$ etc.) where constant in time during a PARANOX run. However, it is not clear, how the solar zenith angle evolved between the examined values θ_0 and θ_5 . Were there some real evolutions corresponding to different release hours and latitudes, as authors state later in Figure 2. caption?

The intervals and used values for the LUT parameters are given in Table 1. The LUT was constructed for every possible combination of these parameters, except for differences larger than 75 degrees between the solar zenith angles (these cannot differ more than 75 degrees in 5 hours), totaling about 10^5 entries. We kept temperature, [O_3] and [NO_x] constant during a PARANOX run. Of course the photolysis rates will change

Table 1. Variables and range used in the construction of the Look-Up Table. θ_0 and θ_5 represent the solar zenith angle at time of release and at the end of the run (5 hours), respectively.

Parameter	**Values used in Look-Up Table**
Temperature (K)	275, 280, 285, 310
$[O_3]$ (ppbv)	5, 20, 35, 75
$[NO_x]$ (pptv)	10, 200, 1000, 2000, 6000
θ_0 ()	-90, -60, -45, -30, -15, 0, 15, 30, 45, 60, 75, 90
θ_5 ()	-90, -60, -45, -30, -15, 0, 15, 30, 45, 60, 75, 90
$J(NO_2)$ (s^{-1})	0.0005, 0.0025, 0.0050, 0.0120
$\frac{J(NO_2)}{J(O(^1D))}$	0.0005, 0.0015, 0.0025, 0.0055

during the 5 hours. We fit a sine function to the solar zenith angles to simulate the variation in the zenith angles, and use this so simulate the variation in the photolysis rates during the 5 hours.

P17800, L22 - P17801, L8: Authors claim that frequency of situations with weak winds, low marine boundary layer, strong emissions leading to saturation effects is small, hence they did not include these parameters in the LUT. However, what about strong winds and strong vertical mixing, how can this influence the plume dilution into the background air, consequently the evolution of chemical species? And what about dry/wet deposition of plume species? As stated at P17794: L14, PARANOX does not consider rainout, does it hold for dry deposition as well? What is the expected effect of these simplifications? Further, why is water vapour not included in the sensitivity analysis? It can have impact on reactions (R1) and (R12) influencing OH radical formation and NO_x nighttime chemistry (HNO_3 formation).

Wind speed indeed influences the dispersion of the plume into background air. We ran simulations for different (strong) wind speeds and found that the fraction of NO_x remaining increases less than 1% when winds increase to speeds $>$ 12 m/s (we use

6 m/s in our LUT). The integrated NOPE increases by about 10% when increasing to speeds $>$ 12 m/s. However, we found by analyzing an ensemble of GEOS-Chem output for grid cells with ship emissions that situations with wind speeds $>$ 12 m/s occur in fewer than 5% of all situations. We acknowledge that not including wind speed as environmental parameters introduces errors, but believe this error to be generally small, as strong wind situations do not occur often.

The PARANOX model does not consider dry or wet deposition. It would be computationally unfeasible to include parameters for wet and dry deposition, as this would further increase the number of parameters in our LUT and would require storage of these parameters during the GEOS-Chem run. Neglecting HNO_3 wet deposition is expected to lead to a high bias on our HNO_3 that is put into GEOS-Chem. However, as the conversion from HNO_3 to NO_x is very slow and the HNO_3 will be removed in GEOS-Chem, we expect that the overall effect on NO_x concentrations is limited. A recent study by Coleman et al. [2010], estimates ozone deposition rates as low as 0.1 ppbv per 5 hours, so the effect of neglecting O_3 dry deposition is very small.

Indeed, water vapour does have an impact on the OH radical formation via reactions R1 and R12. We account for a change in water vapour concentrations as a function of temperature in PARANOX, as mentioned in P17799; L26.

P17802, L6: The depth of the lowermost layer should be specified first here (it is done later at P17805, L11). How can this affect the results? If the lowermost layer is too thin, at certain conditions (higher mixing depths) the ship plume will dilute into higher layer(s) as well within 5 h after release. Emissions in GEOS-Chem were injected always in the lowermost layer? What is vertical model extent (the altitude of the 47th layer?).

We adapted the manuscript and now mention the depth of the lowermost layer, which is 120 m, here. Emissions are always released in this lowest layer, and are mixed rapidly (within 30 minutes) through the boundary layer by the non-local PBL mixing scheme in GEOS-Chem. Furthermore, the horizontal extent of a grid cell (about 200x250 km^2), ensures effective dilution upon emissions. The vertical model extent is 80 km.

P17802, L14-22: Authors state that no daily variation of emissions was considered, only monthly variation in case of EMEP emissions. What about hourly variation, was it considered? if yes, than the original emissions that are reduced have to be those from 5 h before actual model time. This raises also the question of the emissions input frequency.

We assume that ship emissions have no diurnal variation, as ships travel in open sea day and night. No information on diurnal variation of ship emissions is available, if this was the case we would indeed need to make sure the model would reduce the correct emissions.

P17802, L8: Was the spin-up run (2004) common for each experiment or they were all run with spinup, but only the second year of each run (2005) was analyzed? Did this year (2005) represent an average climate or did it encounter some extremities compared to other years?

We performed the spinup for every simulation, and only analyzed the second year (2005). To our knowledge 2005 was a regular year without any extremities (e.g. no El-Niño).

P17804, L1-9: Additional simulations: the 'standard model' is used with no-ship emissions, but why it is not used (as it already suggested in the general comments) with ship emissions as well, to compare it with the new approach and with the instant diluting case (so having 4 simulations: 1 without ship emissions, 3 treating ship emissions in a different way)? Further it is difficult to follow what simulations were performed. It would be helpful to assign ID for each run in a similar way as it was done in e.g. Cariolle et al. (2009) or Huszar et al. (2010). The presented absolute and relative changes than can be explicitly expressed by these IDs.

We now include the comparison with the standard model in our results section, see our result to general comment 2.

P17805,L8 - P17806, L18: I would welcome a more systematic comparison. Authors are presenting first the effect of parameterization on NO_x *in absolute and relative sense for January and July. Why there are no "relative" figures for ozone (only absolute ones)? It would be useful to gain impression of the relative importance of ozone change caused by the parameterization. Further, the effect of ship emissions are presented, but only for summer. Why is winter omitted? At last, in my opinion a more common approach would be to present first the ship emission induced* NO_x *and* O_3 *changes (using either the improved model or the instant diluting one) and than the parameterization's effect, to compare the magnitude of the two (i.e. how the ship induced* NO_x/O_3 *changes are modulated by the parameterization). However, I understand that presenting all these (absolute/relative) differences, including the additional standard model run (see previous comment), eventually vertical crossections, would significantly increase the number of figures. So I at least suggest to show the relative difference of the ozone change due to parameterization and the effect of ship emissions for winter.*

We updated our manuscript and now include the 'relative' difference plots for ozone and discuss the effect of ship emissions in winter.

P17816, Figure 2 and P17817, Figure 3: in the 6th and 7th panel: solar zenith angles 0 - 90 deg correspond to darkness? In text (e.g.P17799, L16) θ_0 *= 10 deg is attributed to noon at low altitudes so this is clearly a mistake and the x-axis have to be relabeled.*

We adapted this figure in our manuscript.

Technical corrections:

P17796, L13-14: Starting at this point the 'fraction of NO_x *remaining' is used trough the whole study. I suggest to use 'remaining fraction of* NO_x*' or 'plume-fraction of* NO_x*'.*

We prefer to continue to use the 'fraction of NO_x remaining', as we want to emphasize the fraction / reduction in the emissions.

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P17790, L7: Here and further in the manuscript the 'in the 5h after the release...' formulation is used. I suggest to use rather 'during the first 5 h after plume release' (like it is used in von Glasgow et al., 2003)

We adapted this in our manuscript.

P17799, L22: the name of the parameter (θ_5) missing

We adapted this in our manuscript.

Figures: I think the spatial figures 6., 7., 8. and 9. can be reduced in size a bit in order that the two sub-figures fit next to each other without loosing the resolution unacceptably. With this, more figures can be showed (as I proposed earlier) without increasing the number of pages significantly.

We reduced the figures in size in our manuscript, so we can show more figures.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 17789, 2011.