

Interactive comment on “On the export of reactive nitrogen from Asia: NO_x partitioning and effects on ozone” by T. H. Bertram et al.

Anonymous Referee #1

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General comments.

This paper is of general interest, presents and interprets field measurements in a new way, and is relevant to ACP. However, it seemed to be hastily written in parts, with some inconsistencies and omissions that will need to be corrected before publication. The abstract claims to “assess the impact of increasing emissions of nitrogen oxides in East Asia on ozone production rates”, but this point is not sufficiently clearly made. At present, the MS quantifies the current state of the atmosphere (as of 2006), and notes that NO_x is increasing over time, but does not explicitly follow through to define the impact of increasing emissions. Unless I have missed a point, I'd recommend expanding on that discussion in the text to better support the statement in the abstract. An earlier study by Hudman et al. (JGR, 2004, doi:10.1029/2004JD004974) reaches fairly similar

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conclusions about ozone formation in trans-Pacific transport. The comments regarding NO_x release from thermal decomposition of PAN following subsidence of dry air are quite consistent with earlier studies that should be better cited throughout. Finally, uncertainties in input parameters are not well treated. I was left wondering how significant the uncertainty of flux calculations based on measured wind speeds, the sensitivity of the box modeling on omitted chemistry of NO₃-mediated reactions after dark, and the dependence of the ozone production crossover point to uncertain acetaldehyde measurements might be. These are minor revisions, but should be addressed before this MS is accepted for publication.

Specific comments.

p. 24956, line 20: presumably reactive nitrogen here and throughout the paper is specific to the gas phase – please clarify

p. 24957, line 3: “NO_x is removed... following the reaction of NO₂ with OH.” This is a convenient simplification; however, on time scales of intercontinental transport and in the absence of wet removal, at least one study has shown HNO₃ photolysis and reaction with OH can be a significant source of NO_x (Neuman et al., 2006, JGR, doi:10.1029/2005JD007010. Section 4.3 in this paper seems to contradict this statement here; please reconsider.

p. 24958, line 13: “. . . HNO₃ is viewed as an irreversible sink for NO_x.” This seems like an overstatement, as in the comment above. Further, in Section 4.3 later in this paper the authors calculate the NO_x source from HNO₃ photolysis and OH reaction. Fig. 7 shows these calculations, which appear to indicate diurnally-averaged HNO₃ decomposition accounts for ~25% of NO_x above 6 km. The daytime contribution from HNO₃ will likely be larger. In fact, p. 24967 line 9 ff states “. . . HNO₃ . . . accounts for nearly 30% of in-situ NO_x production above 5 km.” This seems contradictory. Please reconsider how to more consistently explain the behavior of HNO₃ throughout this paper.

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p. 24960, line 1: "the main transport corridor" is not defined or supported here. What is this, where does it occur in lat-lon-altitude, and is this seasonally dependent? A citation supporting this statement would be relevant here.

p. 24962, line 23: "In the mid troposphere (4-10 km) sum(PNs) comprise as much as 80% of total NO_y." Yet based on 5 airborne studies, most taking place north of 35°N, Parrish et al. (JGR, 2004, doi:10.1029/2003JD004226) found that "HNO₃ generally accounted for one-half to two-thirds of the NO_y" in the free troposphere over the U.S. and North Atlantic. Why the distinct differences between these two studies? Some additional discussion to provide context would be interesting here.

p. 24964, line 18: The box model is constrained by measurements obtained aboard the DC-8. However, the acetaldehyde data are likely key to these calculations but are difficult to measure in flight at low concentrations in the UTLS (www-air.larc.nasa.gov/TABMEP.html). I would suggest a more thorough error analysis would be appropriate here to attempt to quantify the sensitivity of these interpretations to the uncertainties of the underlying data and modeling assumptions.

p. 24964, line 19 ff: Earlier the authors discussed nighttime processing via NO₃, N₂O₅, and chemistry of ClNO₂. This chemistry is fairly complex and provides a potential loss route of NO_x via heterogenous uptake, but seems to be omitted from their box model. Later, the diurnally-averaged model results are presented. It would seem that neglecting potential loss routes after dark, after mentioning them in the introduction, is an oversight that should be addressed before publication.

p. 24966, line 11: Might also note that Parrish et al. calculated an average of 9±4% and suggested that Li et al. was an overestimate of NO_y exported from the North American boundary layer.

p. 24966, line 22: "Particulate nitrate was not included. . ." Can some general statement be made, even with sparse data coverage, to support the unstated but implicit assumption that particulate nitrate was a minor fraction of the gas-phase NO_y?

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p. 24966, line 23: "Based on trajectory analysis..." This point is central to the main conclusions of this section, and would warrant some justification, which is entirely lacking. Can a study be cited here to provide some seasonally-relevant support for this assertion?

p. 24967, line 9 ff: Again, this contradicts earlier statements that suggest NO_x loss to HNO₃ is irreversible. Please reconcile.

p. 24967, line 18: "As a result, we expect. . ." This was a conclusion reached by Hudman et al., JGR, 2004, doi:10.1029/2004JD004974, which should be cited here.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 24955, 2012.

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