Review of Bertram et al., doi:10.5194/acpd-12-24955-2012.

This paper describes measurements of NOy species during INTEX-B, and estimates of NOy export from the Asian continent during that season (Spring). The data could be useful and worth having in the literature, however there are some significant limitations in the interpretation and presentation that need to be addressed. This paper is not publishable in its current form and will need significant modification before it is acceptable.

General Comments:

The authors ignore numerous papers that have looked at the phenomenon they are discussing in this paper: the transport of PANs, subsequent thermal decomposition and production of O_3 from that NOx. The authors make the point several times that their measurements took place in the middle of the Pacific where this PAN => O_3 effect hasn't been looked at before, perhaps as justification for not referencing other key work? Russo et al, [*Russo et al.*, 2003] discuss the long-range transport of PAN out of Asia and show some very interesting PAN (and NOy data). The Jaffe group has published numerous papers on the effects of PAN transported from Asia into the west coast of N. America and the NOx-O_3 chemistry that results ([*Berntsen et al.*, 1999; *Jaffe et al.*, 1999; *R Kotchenruther et al.*, 2001; *R A Kotchenruther et al.*, 2001] just to name a few). Curiously, the authors do reference Hudman et al., who present model results for ITCT 2K2, but the actual observations; Roberts et al., [*Roberts et al.*, 2004] and Nowak et al, [*Nowak et al.*, 2004] were not mentioned. Another aspect of this transport that was not really mentioned was that it tends to be episodic, as it is driven by large-scale warm conveyer-belt weather systems. It would be interesting to know if any such episodes were observed in this study and how their frequency and magnitude might affect the flux estimated presented here.

The paper lacks the context of previous measurements and analyses (because it doesn't mention them), there is a lack of connection between the general point of this paper, and the general concept of increasing Asian NOx affecting the North Pacific and North America. This has been discussed by Parrish et al., [*Parrish et al.*, 2004] and the Jaffe group, among others. How do the conclusions in this paper fit in with those analyses? We get no sense of what the bigger picture looks like.

The authors seem to be aware of PAN photolysis and mention it some times, and then forget about it at others. Basically, PAN photolysis is what limits PAN/NOy ratios at higher altitudes, that, and the fact that the thermal lifetime becomes so long that transport (i.e. vertical exchange times) in and out of the upper troposphere are shorter than the thermal lifetime, control PAN vertical profiles above about 7 km. The bottom line is that the paper needs to be consistent on this point.

Specific Comments:

Page 24956, line 20-21. PAN, alkyl nitrates, and HNO_3 are not "oxides of nitrogen".

Page 24957, line 2. What is a "permanent NOx reservoir"? Don't you mean "NOx sink"?

Page 24957, lines 10-23. This discussion is not clear, in fact if I didn't already know the chemistry, I would be completely confused. Reactions 4 and 5 do not constitute NOx losses unless either NO_3 reacts with something to form HNO_3 or an organic nitrate, or N_2O_5 reacts with a surface and is lost. The sentence on lines 17-19 "This loss process occurs primarily at night due to the strong visible light absorption and subsequent dissociation of NO_3 as well as rapid reaction with NO (which is significantly reduced at night)." is nonsense. Really? strong visible light absorption at night??? The authors have combined several ideas, put them in one sentence, and ended up with something completely misleading.

Page 24958, line 9. The Talukdar et al., paper is about PAN-OH reaction rates and PAN photolysis, not thermal decomposition. An appropriate reference would be either the Kirchner et al. review article [*Kirchner et al.*, 1999], or the IUPAC compendium.

Page 24958, line 25-30. This paragraph is misleading. NOy in the free troposphere is known to be mostly PAN and HNO_3. There are a lot of observations (many more than summarized in the 2 references given). The reasons for this are partly given in this paragraph, but the main reason is that PAN and HNO_3 are longer lived than NOx (or any of the other oxides of nitrogen such as NO_3 and N_2O_5).

Page 24959. Line 2. I've looked through Day et al. 2003 (the citation of which is messed up, see below) and there are no free troposphere measurements that I could see.

Page 24961. It sounds like the TD-LIF inlet is a single tube that is temperature programed. Is that true? I can't tell from what is presented here. If so what was the program (time at each temperature etc.). On what basis do the authors conclude that $ClNO_2$ would have been observed in the ΣPNs channel? Thaler et al., [*Thaler et al.*, 2011] show that $ClNO_2$ decomposition is very close to that of methyl nitrate, implying the $ClNO_2$ would be detected in the ΣANs channel.
What does particle nitrate do in your system? How do you know what it does, what tests did you do on it?
There is no discussion of the particle NO_3^- measurements - this needs to be added.
There was an instrument intercomparison that was part of the INTEX-B project. How did that turn out for the various measurements?

Page 24962. Line 13. "The small set of previous observations of NOy in the Pacific" How about some references here.

Page 24962. Line 26. The authors seem to be saying that there is net PAN production in the upper troposphere, similar to that modeled by Staudt et al., [*Staudt et al.*, 2003]. Does the chemical modeling show that?

Page 24964. Line 14. You are using measured OH and HO_2 to calculate O_3 Production and Loss? Those measurements are not described anywhere in this paper. This needs to be corrected.

Page 24965 last few lines, Page 24966 first lines. These NOx flux measurements should be in the same units. Also, what does Tg NOx mean? What is the molecular weight of NOx? 30?, 46?, 38 g/mole?

Page 24966. Line 7. 8 to 10% of what?

Page 24966. Line 23-24. It seems important to show, or to cite a study showing, that the majority of lofted Asian emissions go through the "window" defined by in Figure 6. To just state that here, un-supported is not acceptable.

Page 24966 line 27. Do you have independent evidence of Siberian biomass burning?, HCN, CH_3CN measurements?

Page 24967. Section 4.3 Please justify including HNO_3 photolysis and ignoring PAN photolysis.

Page 24967. Section 4.4 and Figure 8 through Page 24968. This doesn't seem to make sense. I always thought that $O^1D + H_2O$ made radicals (2OH radicals in fact), which, in the presence of sufficient VOC and NOx, made O_3. Now you are saying H_2O somehow interferes with O_3 production? How can that be? Also, if you look at Figure 8 (which needs to be larger) there is a population of points at higher H_2O for which O_3 production is high - isn't that what you'd expect? The points that show apparent higher O_3 production at lower H_2O are suspect because your relatively crude filter for stratospheric influence will still leave points that are higher in O_3 and low in H_2O, precisely the points that the authors are focusing on.

Page 24968, Line 18. Define "extreme sensitivity" Extreme compared to what?

References

The doi numbers on the two Day et al. references are messed up.

Figures.

Figure 5 – the individual points are hard to see.

Figure 6 – Can't read the labels on the color scale.

Figure 7 – The numbers on the log axes are hard to read.

Figure 8 – These figures need to be larger.

References used in this review

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