

Interactive
Comment

Interactive comment on “Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China” by J. B. Zhang et al.

J. B. Zhang et al.

jbzhang6102@sina.com

Received and published: 5 June 2011

Thanks for your suggestive comments. We have reviewed the published papers on PANs. Indeed, most of your comments contribute our improvement of the full-text. Therefore, we have made corresponding revisions and responses as follows. First of all, the reviewer has mentioned that the nighttime loss of PAN and PPN has a large component that is caused by deposition to surface. However, he or she failed to make a link with the full-text about this statement. Namely, we can hardly find out the conflict between the full-text and the reviewer's statement. Secondary, we have updated the literature and related citations have been added in Table 1.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Page 8177, Lines 20-28: For the configuration of PPN's retention time, we used aqueous PPN as a volatile source to make sure its gaseous retention time when it is detected by GC-ECD. , For PPN, the relative response value was used for its quantification. Since the PAN instrument used in this campaign was borrowed from Roberts and his colleagues. The PAN instrument has been used in a number of studies (Roberts et al., 2002; Roberts et al., 2001; Roberts et al., 2007; Roberts et al., 1998). It has been calibrated in lab before and after its running in this campaign. Therefore, the relative response value used in this study is reliable.

Page 8178: Since it is a group campaign, with the consideration about the specific focus on PANs studies, we have briefly introduced the sampling parameters of O3 and other air pollutants. The details can be reviewed in other related studies (Shao et al., 2009; Wang et al., 2010). The mechanism of O3 and NO/NO2/NOx detection are based on ISO10313 chemical luminescence method and ISO7996 chemical luminescence method, respectively. Therefore, the reported NOx by this instrument contains PANs (PAN, PPN, MPAN, etc). During the campaign, there is also a NOy instrument, its value is almost higher than that of NOx instrument. Therefore, the reported NOx by above mentioned instrument was not the value of NOy as the reviewer addressed.

For Page 8180 Lines 28-29: The author addressed there were more compounds that contribute to PAN and PPN formation than the ones listed in the full-text. We agree with the reviewer's comments. A good review on PAN (Altshuller 1993) has provided a comprehensive summary on PAN. However, in this study, we would like to typically focus on PANs atmospheric behavior. Since we have not simultaneously measured their specific VOCs precursors, our present efforts are to investigate their own behaviors and their relationship with total VOCs as a preliminary study. Nonetheless, maybe in the further study, we will try to conduct closure experiment to specifically focus on their VOCs precursors as listed in published review (Altshuller 1993).

Section 3.2 We agree with the reviewer's comments that the planetary boundary layer also plays an important role in the morning's PANs variation. However, it is hard to com-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



pletely conclude the morning rise of PANs just by planetary boundary layer changes. To the best of our knowledge, during the sunrise and increased emission of NO_x and VOCs, it should be a major role in contributing the increase of PANs. In addition, there are a number of studies (Ciccioli et al., 1988; Granby et al., 1997; Matsui et al., 2010; Pippin et al., 2001; Shepson et al., 1991; E. J. Williams et al., 1997) have also provided the similar reasons for the increase of secondary photochemical pollutants. Therefore, our statement that the morning rise of PANs concentrations relates to the sunrise and increased emission of primary pollutants cannot be neglected. The reviewer indicated that PANs can deposit on ground surfaces, there is a lack of fraction for this sink. Based on our discussion with the group who is in charge of NO_x measurement, the potential of fresh emission at that time can be excluded.

Page 8183, Lines 2-3: The ratio of PAN/PPN is a good indicator to identify anthropogenic control and natural hydrocarbon control. This theory has been well established in a number of studies (Roberts et al., 2001; Roberts et al., 2003; Roberts et al., 2007; J. Williams et al., 2000; J. Williams et al., 1998). Interesting, the reviewer also used Roberts' publication to deny the correctness of the ratio of PAN/PPN as a useful way to preliminary judgment tool. In particular, the reviewer also mentioned that isoprene was a source of PAN but not PPN. It is really the case. However, meanwhile, we also should be neglect that isoprene is also a source of other OVOCs (Duane et al., 2002; Grosjean et al., 1993; Nouaime et al., 1998; Shao 2002; Xie et al., 2008). The fraction of isoprene contributes to PAN formation is complex and problematic. In addition, the source of isoprene is not only just from natural emission.

Page 8184: The reference of Jia et al., 2006 was not cited and will be deleted from the full-text. The discussion about the heterogeneous reactions of PAN and PPN is a preliminary conclusion based on our observation. It has been further investigated in another study (Xu and Zhang 2011).

Page 8185 Line 15: acetyl-perxynitrite will be modified by peroxyacetyl radical.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Page 8186: The pressure dependent equations listed here is just to provide complete information about PPN's thermal behavior. For further calculation, we also found the pressure variation was not that significantly important in this study. The thermal decomposition rate constants of PAN was depended by local temperature and on the concentration ratio of NO to NO₂, therefore, the differences between this study obtained value and the value in (Kirchner et al., 1999) is reasonable. Whatever, there is only slightly different. Page 8188, lines 3-4: the reviewer has neglected the balance of precursor ratio and temperature. Both of them play a role in PAN or PPN formation conversely, namely, with the consideration of the importance of temperature on PAN or PPN formation, NO reaction is more important for PPN. For the part of TDPAN and TDPPN, we have provided detailed steps on its calculation in the section of 3.4. The equations are listed as follows and details about the calculation have been described in the full-text. The main concept for these mathematical calculations has been well established in a number of published references (Grosjean et al., 1994a; Grosjean et al., 1994b; Mineshos and Glavas 1991; Roumelis and Glavas 1992. see Fig PAN generation 1 and 2).

For Figures, we agree with the reviewer's suggestions. We would like to enlarge the figures with the help of the publishing staff and workers. Thanks for your kind comments for the improvement of our study.

References: Altshuller, A. P.: PANs in the Atmosphere, Journal of the Air & Waste Management Association, 43, 1221-1230, 1993. Ciccioli, P., Cecinato, A., Brancaleoni, E., Brachetti, A.: Seasonal and Diurnal-Variations of Peroxyacetyl Nitrate (Pan) in a Suburban Area of Central Italy and Their Relation with the Meteorological Conditions and the Concentration of Other Photochemical Oxidants and Their Precursors, Abstracts of Papers of the American Chemical Society, 196, 61-Envr, 1988. Duane, M., Poma, B., Rembges, D., Astorga, C., Larsen, B. R.: Isoprene and its degradation products as strong ozone precursors in Insubria, Northern Italy, Atmospheric Environment, 36, 3867-3879, 2002. Granby, K., Egelov, A. H., Nielsen, T., Lohse, C.: Carboxylic

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

acids: Seasonal variation and relation to chemical and meteorological parameters, *Journal of Atmospheric Chemistry*, 28, 195-207, 1997. Grosjean, D., Grosjean, E., Williams, E. L.: Thermal-Decomposition of Pan, Ppn and Vinyl-Pan, *Journal of the Air & Waste Management Association*, 44, 391-396, 1994a. Grosjean, D., Williams, E. L., Grosjean, E.: Atmospheric Chemistry of Isoprene and of Its Carbonyl Products, *Environmental Science & Technology*, 27, 830-840, 1993. Grosjean, D., Williams, E. L., Grosjean, E.: Gas-Phase Thermal-Decomposition of Peroxy-N-Butyryl Nitrate, *International Journal of Chemical Kinetics*, 26, 381-387, 1994b. Kirchner, F., Mayer-Figge, A., Zabel, F., Becker, K. H.: Thermal stability of peroxy nitrates, *International Journal of Chemical Kinetics*, 31, 127-144, 1999. Matsui, H., Koike, M., Kondo, Y., Takegawa, N., Kita, K., Miyazaki, Y., et al.: Spatial and temporal variations of aerosols around Beijing in summer 2006: Model evaluation and source apportionment, *Journal of Geophysical Research - Part D - Atmospheres*, D00G13 (22 pp.), 2010. Mineshos, G., Glavas, S.: Thermal-Decomposition of Peroxypropionyl Nitrate - Kinetics of the Formation of Nitrogenous Products, *Reaction Kinetics and Catalysis Letters*, 45, 305-312, 1991. Nouaime, G., Bertman, S. B., Seaver, C., Elyea, D., Huang, H., Shepson, P. B., et al.: Sequential oxidation products from tropospheric isoprene chemistry: MACR and MPAN at a NO_x-rich forest environment in the southeastern United States, *Journal of Geophysical Research-Atmospheres*, 103, 22463-22471, 1998. Pippin, M., Bertman, S., Thornberry, T., Town, M., Carroll, M. A., Sillman, S.: Seasonal variations of PAN, PPN, and O-3 at the upper Midwest PROPHET site, *Journal of Geophysical Research-Atmospheres*, 106, 24451-24463, 2001. Roberts, J. M., Flocke, F., Stroud, C. A., Hereid, D., Williams, E., Fehsenfeld, F., et al.: Ground-based measurements of peroxy-carboxylic nitric anhydrides (PANs) during the 1999 Southern Oxidants Study Nashville Intensive, *Journal of Geophysical Research-Atmospheres*, 107, ACH 1-1, 2002. Roberts, J. M., Flocke, F., Weinheimer, A., Tanimoto, H., Jobson, B. J., Riemer, D., et al.: Observations of APAN during TexAQS 2000, *Geophysical Research Letters*, 28, 4195-4198, 2001. Roberts, J. M., Jobson, B. T., Kuster, W., Goldan, P., Murphy, P., Williams, E., et al.: An examination of the chemistry of per-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

oxycarboxylic nitric anhydrides and related volatile organic compounds during Texas Air Quality Study 2000 using ground-based measurements, *Journal of Geophysical Research-Atmospheres*, 108, ACH4(1-12), 2003. Roberts, J. M., Marchewka, M., Bertman, S. B., Sommariva, R., Warneke, C., de Gouw, J., et al.: Measurements of PANs during the New England air quality study 2002, *Journal of Geophysical Research-Atmospheres*, 112, 1-14, 2007. Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., et al.: Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: Implications for regional ozone production from biogenic hydrocarbons, *Journal of Geophysical Research-Atmospheres*, 103, 22473-22490, 1998. Roumelis, N., Glavas, S.: Thermal-Decomposition of Peroxyacetyl Nitrate in the Presence of O₂, NO₂ and NO, *Monatshefte Fur Chemie*, 123, 63-72, 1992. Russo, R. S., Talbot, R. W., Dibb, J. E., Scheuer, E., Seid, G., Jordan, C. E., et al.: Chemical composition of Asian continental outflow over the western Pacific: Results from Transport and Chemical Evolution over the Pacific (TRACE-P), *Journal of Geophysical Research-Atmospheres*, 108, 2003. Shao, M.: Biogenic isoprene emission mechanism from (CO₂)-C-13 exposure experiments, *Chinese Chemical Letters*, 13, 897-900, 2002. Shao, M., Zhang, Y. H., Zeng, L. M., Tang, X. Y., Zhang, J., Zhong, L. J., et al.: Ground-level ozone in the Pearl River Delta and the roles of VOC and NO_x in its production, *Journal of Environmental Management*, 90, 512-518, 2009. Shepson, P. B., Hastie, D. R., Schiff, H. I., Polizzi, M., Bottenheim, J. W., Anlauf, K., et al.: Atmospheric Concentrations and Temporal Variations of C-1 C-3 Carbonyl-Compounds at 2 Rural Sites in Central Ontario, *Atmospheric Environment Part a-General Topics*, 25, 2001-2015, 1991. Wang, B., Shao, M., Roberts, J. M., Yang, G., Yang, F., Hu, M., et al.: Ground-based on-line measurements of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in the Pearl River Delta, China, *International Journal of Environmental Analytical Chemistry*, 90, 548-559, 2010. Williams, E. J., Roberts, J. M., Baumann, K., Bertman, S. B., Buhr, S., Norton, R. B., et al.: Variations in NO_y composition at Idaho Hill, Colorado, *Journal of Geophysical Research-Atmospheres*, 102, 6297-6314, 1997. Williams, J., Roberts, J.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

M., Bertman, S. B., Stroud, C. A., Fehsenfeld, F. C., Baumann, K., et al.: A method for the airborne measurement of PAN, PPN, and MPAN, *Journal of Geophysical Research-Atmospheres*, 105, 28943-28960, 2000. Williams, J., Roberts, J. M., Fehsenfeld, F. C., Bertman, S. B., Buhr, M. P., Goldan, P. D., et al.: Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, *Geophys. Res. Lett.*, 24, 1099-1102, 1998. Xie, X., Shao, M., Liu, Y., Lu, S. H., Chang, C. C., Chen, Z. M.: Estimate of initial isoprene contribution to ozone formation potential in Beijing, China, *Atmospheric Environment*, 42, 6000-6010, 2008. Xu, Z. Q., Zhang, J. B.: PAN, PPN, and MPAN episodes during the photochemical smog season in Beijing, China, *Atmospheric Chemistry and Physics*, Submitted, 2011.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 8173, 2011.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

/srv/www/htdocs/tmp/414332153/figure-1.pdf

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Fig. 1. Table 1

Interactive
Comment

/srv/www/htdocs/tmp/414332153/figure-2.pdf

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Fig. 2. PAN generation1

Interactive
Comment

/srv/www/htdocs/tmp/414332153/figure-3.pdf

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Fig. 3. PAN generation 2