

Response to referee #1

The comments from the anonymous referee #1 are hard to accept. He suggested rejecting our study with limited statements. We would like to response to the referee point by point as follows:

1. Seemingly, we not only choose a new location to study the atmospheric behavior of PANs, but also we have comprehensively investigated on them and pointed out the potentials of heterogeneous reactions of PANs with particles. As mentioned by the referee #1, there are some recent papers took a comprehensive look at PANs, however, there is a lack of efficient information about the field study in metropolis city, China (Wang et al., 2010; Xue et al., 2011; J. M. Zhang et al., 2009). Along with the quick development of Beijing and its rapid increase of population, there is a great necessity to make clear about its photochemical pollution. However, there is limited information after 1990s (Zhang and Tang 1994). ACP is a leading journal in atmospheric studies and attracts many colleagues in this area. We would like to share our understanding about PANs pollution in China, which is also the first time of PANs pollution about Beijing published internationally. It not only can call for the authority's focus on this growing issue and to put efforts to control, but also arouses more researchers' interests on PANs study, especially for its increasing trend in developing countries. In developed countries, PANs might not be a problem. However, it is really a potential issue here.
2. Unfortunately, the second point addressed by the referee #1 was hard to follow. Please try to re-arrange your expression. However, we still can provide some reply for your consideration. The model used in this study has been verified in a number of studies (Lee and Kinsley 1988; Malanca et al., 2009; Mineshos and Glavas 1991; Moise et al., 1999; Seefeld and Kerr 1997).

The kinetics applied in this study is not site specific. Therefore, I am just doubt whether there is a necessity to re-do the experiments in lab, since this part has been fully investigated in other studies (Malanca et al., 2009; Moise et al., 1999; Seefeld and Kerr 1997).

3. In this study, we tried to add a link between PANs concentration with particles, since there is so limited investigation about its surface chemistry (Birmili et al., 2009; Gamblin et al., 2006). Therefore, we developed related figures. Based on the measurement data and statistical analysis, we cannot neglect the effects of particles on PANs chemistry. Therefore, we promoted our idea that the heterogeneous reaction of PANs on particle surface might be a way of its atmospheric cycling. In this study, it mainly focused on filed campaign. Lab-based thorough investigation might be another topic which is beyond this study.
4. The approach of correlation used in this study has been widely used in atmospheric researches. Since the variations of atmospheric chemicals (or particles) day by day were different (statistically significant), it was a general understanding in atmospheric sciences (Chow et al., 1998; Ciccioli et al., 1988; Hastings et al., 2004; Hess et al., 1996; Legrand and Deangelis 1995; Pippin et al., 2001; Shepson et al., 1991; Williams et al., 1997). Therefore, to undertake statistical analysis about the correlation is not meaningful.

Furthermore, we are so interested about any suggestive comments on improving our studies on PANs, which is also good for matching the quality of ACP.

References:

- Birmili, W., Ries, L., Sohmer, R., Anastou, A., Sonntag, A., Konig, K., et al.: Fine and ultrafine aerosol particles at the GAW station Schneefernerhaus/Zugspitze, *Gefahrstoffe Reinhaltung Der Luft*, 69, 31-35, 2009.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., Egami, R. T., Solomon, P. A., Thuillier, R. H., et al.: Spatial

- and temporal variations of particulate precursor gases and photochemical reaction products during SIVAQS/AUSPEX ozone episodes, *Atmospheric Environment*, 32, 2835-2844, 1998.
- 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.
- Gamblin, B., Toon, O. B., Tolbert, M. A., Kondo, Y., Takegawa, N., Irie, H., et al.: Nitric acid condensation on ice: 1. Non-HNO₃ constituent of NO_y condensing cirrus particles on upper tropospheric, *Journal of Geophysical Research-Atmospheres*, 111, -, 2006.
- Hastings, M. G., Steig, E. J., Sigman, D. M.: Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: Implications for the study of nitrate in snow and ice cores, *Journal of Geophysical Research-Atmospheres*, 109, -, 2004.
- Hess, P. G., Srimani, N., Flocke, S. J.: Trajectories and related variations in the chemical composition of air for the Mauna Loa observatory during 1991 and 1992, *Journal of Geophysical Research-Atmospheres*, 101, 14543-14568, 1996.
- Lee, Y. N., Kinsley, M. T.: Kinetics of Peroxyacetyl Nitrate (Pan) Hydrolysis and Its Atmospheric Implications, *Abstracts of Papers of the American Chemical Society*, 196, 179-PHYS, 1988.
- Legrand, M., Deangelis, M.: Origins and Variations of Light Carboxylic-Acids in Polar Precipitation, *Journal of Geophysical Research-Atmospheres*, 100, 1445-1462, 1995.
- Malanca, F. E., Fraire, J. C., Arguello, G. A.: Kinetics and reaction mechanism in the oxidation of ethyl formate in the presence of NO₂: Atmospheric implications, *Journal of Photochemistry and Photobiology a-Chemistry*, 204, 75-81, 2009.
- 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.
- Moise, T., Denzer, W., Rudich, Y.: Direct kinetics study of the reaction of peroxyacetyl radical with NO between 218 and 370 K, *Journal of Physical Chemistry A*, 103, 6766-6771, 1999.
- Pippin, M., Bertman, S., Thornberry, T., Town, M., Carroll, M. A., Sillman, S.: Seasonal variations of PAN, PPN, and O₃ at the upper Midwest PROPHET site, *Journal of Geophysical Research-Atmospheres*, 106, 24451-24463, 2001.
- Seefeld, S., Kerr, J. A.: Kinetics of the reactions of propionylperoxy radicals with NO and NO₂: Peroxypropionyl nitrate formation under laboratory conditions related to the troposphere, *Environmental Science & Technology*, 31, 2949-2953, 1997.
- 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.
- Xue, L. K., Wang, T., Zhang, J. M., Zhang, X. C., Deliger, Poon, C. N., et al.: Source of surface ozone and

reactive nitrogen speciation at Mount Waliguan in western China: New insights from the 2006 summer study, *Journal of Geophysical Research-Atmospheres*, 116, 2011.

Zhang, J. B., Tang, X. Y.: Atmospheric PAN measurements and the formation of PAN in various systems, *Environmental Chemistry*, 1, 30-39, 1994.

Zhang, J. M., Wang, T., Ding, A. J., Zhou, X. H., Xue, L. K., Poon, C. N., et al.: Continuous measurement of peroxyacetyl nitrate (PAN) in suburban and remote areas of western China, *Atmospheric Environment*, 43, 228-237, 2009.