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Simultaneous measurements of peroxyacetyl nitrate and peroxyacetic acid by Chemical Ionization Mass Spectrometry (CIMS): contrasting boreal forest with rural continental Europe

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The peroxyacetyl radical (PA) is formed via the photochemical oxidation of a number of different VOCs. PA radical acts as the source of peroxyacetyl nitrate (PAN), via the reaction with NO_2, and peroxyacetic acid (PAA), via reaction with the HO_2 radical. PAN can act as a temporary reservoir of both PA radical and NO_2 transporting NO_x far from source regions, whereas PAA lifetimes, dominated by deposition, are shorter. We present simultaneous measurements of PAN and PAA in different environments and study the chemistry of the PA radical in contrasting chemical and meteorological conditions.

PAN and PAA were measured simultaneously using CIMS during two field intensives with contrasting meteorological and chemical conditions. The HUMPPA-COPEC 2010 campaign took place during July-August 2010 at the SMEAR II field site, located in boreal forest near Hyytiälä, Finland [1]. The campaign was characterised by above average temperatures with large emissions of BVOCs from the boreal forest. The Particles and Radicals: Diel observations of the impact of urban and biogenic Emissions (PARADE) campaign took place during August-September 2011 at the mountaintop fieldsite on the Kleiner Feldberg, Hessen, Germany, approximately 10 km north of Frankfurt. Temperatures were markedly lower during PARADE compared to HUMPPA and the site had much lower impact from VOCs and a much larger impact from anthropogenic emissions.

PAA was found to be a large proportion of $\Sigma PA_{(PAA+PAN)}$ during the HUMPPA campaign, approaching 50% on occasion. In addition, PAA was found to make up a significant fraction of the total organic peroxides. In contrast, $\Sigma PA_{(PAA+PAN)}$during PARADE was dominated by PAN reflecting the lower temperatures and NO_x levels.

[1] J. Williams et al, 2011, Atmos. Chem. Phys., 11, 10599-10618