



Variation of Tropospheric Hydrogen Peroxide and Formaldehyde From the Subtropics to the Boreal Forest in Europe

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The photochemistry of hydrogen peroxide (H_2O_2) and formaldehyde (HCHO) mediates the budget of HO_x ($= \text{OH} + \text{HO}_2$) and thus has a strong impact on ozone (O_3) and NO_x ($= \text{NO} + \text{NO}_2$) in the troposphere. Three field campaigns at different latitudes in Europe aimed to a better understanding of these processes: DOMINO 2008 (Diel Oxidant Mechanisms In Relation to Nitrogen Oxides) near Huelva (Spain), HUMPPA 2010 (Hyytiälä United Measurements of Photochemistry and Particles in Air) in Hyytiälä (Southern Finland) and PARADE 2011 (Partices and Radicals: Diel Observations of the impact of Urban and Biogenic Emissions) on the Kleiner Feldberg near Frankfurt am Main (Germany). The former represents subtropical winter ($37^\circ 5' \text{ N}$, maritime and urban), the second boreal summer ($61^\circ 51' \text{ N}$, biomass burning events) and the latter summer in a moderate climate zone ($50^\circ 13' \text{ N}$, 826 m.a.s.l., arborous and rural). During the field studies mixing ratios of gas-phase hydrogen peroxide and formaldehyde were measured in-situ between 8 and 21 m above ground level via two slightly changed commercial instruments (Model AL2021 respectively AL4021, Aero-Laser GmbH, Garmisch-Partenkirchen, Germany).

In all data sets H_2O_2 followed clear diurnal patterns whereas HCHO showed smoother variations. However, absolute mixing ratios and daily extremes revealed the different regimes. During DOMINO lowest H_2O_2 was observed at 8:00 UTC (0.045 ppbv) with a maximum at 18:30 UTC (0.15 ppbv). On the contrary, HUMPPA data showed generally higher mixing ratios and time shifted extremes (low 5:00 UTC, 0.17 ppbv and high at 13:00 UTC, 1 ppbv). Although also having a minimum in the morning (8:30 UTC, 0.3 ppbv), peak values during PARADE were observed around midnight (0:00 UTC, 0.6 ppbv).

Values of HCHO showed a similar behaviour for all three data sets with minimums in the early morning while maximums were observed in the afternoon: DOMINO (7:30 UTC, 0.27 ppbv and 18:30 UTC, 1.3 ppbv), HUMPPA (5:30 UTC, 0.25 ppbv and 7:30-15:00 UTC, 0.6 ppbv) and PARADE (7:00 UTC, 1.5 ppbv and 14:00 UTC, 2.3 ppbv). One exception is the high absolute amount during PARADE indicating a direct transport of HCHO from urban areas.

By additional inclusion of campaign averages of O_3 and NO_x , HUMPPA indicates a pristine site even in consideration of some biomass burning events. In contrast, the DOMINO data clearly shows anthropogenic influences, whereas the PARADE mountain site party lies in an urban pollution efflux plume.