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Assessment of the applicability of NO-NO_2-O_3 photostationary state to long-term measurements at the Hohenpeissenberg GAW Station, Germany

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Abstract. Continuous measurements of concentrations of reactive gases, radiation, and meteorological parameters are carried out at the Meteorological Observatory Hohenpeissenberg (MOHp) as part of the Global Atmosphere Watch (GAW) Program. NO, NO_2, O_3 and J_{NO2} data from a four-year period (March 1999-December 2002) are evaluated for consistency with photochemical steady state (PSS, Φ=1) conditions. The extent of deviation from PSS reveals a strong dependence on wind direction at the station. Median values of Φ in the south sector are in the range of 2.5-5.7 and show a high variability. In contrast, values for the other directions show a relatively low variability around a median level of 2. When taking into account peroxy radical concentrations (Φ_{ext}=1) PSS was reached in 13-32% of all cases for the years 1999-2002.
The differences in wind sectors can be explained by local effects. It is shown that the height of the sample inlet line, its distance to the forest and the surrounding topography has a strong impact on both the absolute and relative deviations from PSS. Global irradiance and thus, photolysis of NO_2 is reduced within the dense forest. Since the reaction of NO with O_3 is still proceeding under these conditions, increased NO_2/NO ratios are produced locally in air which is transported through the forest and advected to the MOHp site.

Estimates of the peroxy radical concentration (RO_2) inferred from PSS are compared with peroxy radical measurements made at the site in June 2000 during a three-week campaign. The PSS derived RO_2 levels were higher than corresponding measured levels by at least a factor of 2-3. This analysis was made for a wind sector with minimal local effects on PSS. Thus the corresponding Φ median of 2 can be regarded as an upper limit for a deviation from PSS due to chemical reactions, i.e. by peroxy radicals and possible other oxidants converting additional NO to NO_2.

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