Monitoring of the NO_x/O_3 Photostationary State: Local Impacts or Systematic Deviations?

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Continuous measurements of reactive gases, irradiation, and meteorological parameters are carried out at the Meteorological Observatory Hohenpeissenberg (MOHp) as part of the Global Atmosphere Watch (GAW) Program. In this paper 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) conditions.

The extent of deviation from PSS reveals a strong dependence on wind direction at the station. Median values of ϕ ($\phi = J_{NO2}\cdot[NO_2]/k_1[O_3][NO_2]$) 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 (Figure 1). Generally, the frequency, when PSS is reached, is very low (on average less than 20% during the 4-year period). The differences in wind direction and the general large deviation from PSS can be explained by local effects. It was observed that the height of the sample inlet line, its distance from the forest, and the surrounding topography have a strong impact on the deviation from PSS. For air masses transported through the forest, photolysis of NO_2 is reduced and locally increased NO_2/NO ratios are measured at the nearby site. It should be noted that the surrounding at MOHp is not unusual for ground sites. The results found in this study are, therefore, of general importance for ground stations at which deviations from PSS are observed.

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 3-week campaign. The PSS derived RO_2 levels were higher than corresponding measured levels by a factor of 2-3 (Figure 2). 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 because of chemical reactions, i.e., by the sum of peroxy radicals and possible other oxidants converting additional NO to NO_2.

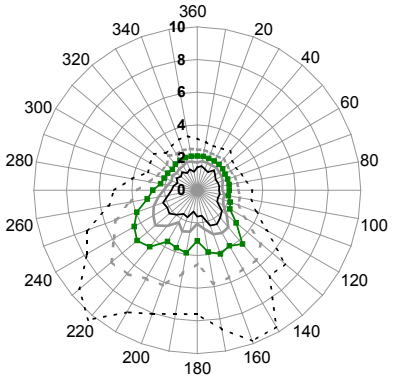

Figure 1. Dependence of ϕ on wind direction for 2000. Only data with $J_{NO2}>6\cdot10^{-3}$ s^{-1} are considered. Green Line: median, other lines: 5, 20, 80 and 95 percentiles, respectively.

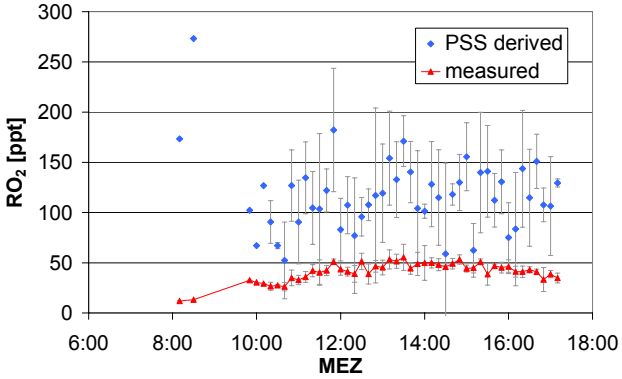

Figure 2. Mean diurnal variation of measured and PSS derived RO_2 radicals for June 18 to July 6, 2000. Error bars refer to the 1σ standard deviation.