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Nitrogen Oxides Measurements at rural Sites in Switzerland: Bias of conventional Measurement Techniques

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Atmospheric odd nitrogen (NOx = NO + NO2) is often measured using commercial instruments with molybdenum converters. NO2 is catalytically converted to NO on a heated molybdenum surface and then measured as NO by chemiluminescence after reaction with ozone. The drawback of this technique is that other oxidized nitrogen compounds such as peroxyacetyl nitrate (PAN) and nitric acid (HNO3) are also partly converted. Thus, NO2 measurements are often overestimated due to interferences of other oxidized nitrogen compounds, especially when measuring photochemically aged air masses. However, molybdenum converters are widely used and a dense network of NO2 measurements exists mainly in polluted environments. Data of these networks may become valid ancillary information for the validation of space-borne data.

This work presents NO2 measurements using different techniques at two rural sites of the Swiss National Air Pollution Monitoring Network (NABEL). The data were recorded at Taenikon (47º 29'N, 8º 54'E, 540 m above sea level), a rural site with moderate population on the Swiss Plateau, and at Rigi (47˚04' 8˚27'57, 1030 m above sea level), a rural elevated station with patches of wood and grasslands in the vicinity.

At Taenikon, ongoing measurements of NO2 started in 1991 using commercial instruments with molybdenum converters. In addition, a CRANOX system with a photolytic converter which is a highly specific technique for NO2 was run from January 1995 to August 2001. Differential Optical Absorption Spectroscopy (DOAS) was used for open path NO_2 measurements from January 1995 to April 1998. In addition, PAN measurements with gas chromatography were performed from April 1995 to November 1996.

At Rigi, simultaneous measurements of NO_2 with both molybdenum converter and photolytic converter are available from November 2001 until now.

The differences in the NO_2 concentrations will be quantified for the two mid-latitude rural stations depending on different environmental conditions. The results will allow estimating the influence of interfering compounds on NO_2 measurements performed with commercial monitors. In the boundary layer, the absolute NO_2 discrepancy of the two different converter techniques is highest in winter due to the generally higher concentrations. On a relative scale, the molybdenum converter instruments overestimate the NO_2 concentrations most during spring/summer due to higher solar input and more prevalent photochemistry. These interferences have to be considered when such data is used for ground-truthing of satellite data or the validation of chemical transport models.