Continuous Nitrogen Oxides Measurements at Rural Sites in Switzerland: Bias of Conventional Measurement Techniques

M. Steinbacher[1], C. Zellweger[1], C. Hüglin[1], B. Schwarzenbach[1], S. Bugmann[1], C. Ordonez[2], A. S. H. Prevot[2]

[1] Swiss Federal Institute for Materials Science and Technology (EMPA), Laboratory for Air Pollution/Environmental Technology, Duebendorf, Switzerland
[2] Paul Scherrer Institut, Laboratory of Atmospheric Chemistry, Villigen, Switzerland

EMPA
Materials Science & Technology

Introduction

Atmospheric odd nitrogen (NO_x = NO + NO_2) is often measured using commercial instruments with molybdenum converters. NO_2 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 (HNO_3) are also partly converted [1]. Thus, NO_2 measurements are often overestimated due to interferences, especially when measuring photochemically aged air masses. However, molybdenum converters are widely used and a dense network of NO_2 measurements exists mainly in polluted environments. Data of these networks may become valid ancillary information for the validation of space-borne data. We compared perennial NO_2 data using a molybdenum converter with NO_2 concentrations gathered with a photolytic converter that is a highly specific technique for NO_2.

Study Sites/ Experimental

The data were recorded at Taenikon (47° 29'N, 8° 54'E, 540 m asl), a rural site with moderate population on the Swiss Plateau, and at Rigi (47°04' 8°27'57, 1030 m asl), a rural elevated station with patches of wood and grasslands in the vicinity.
NO_2 measurements with a photolytic converter (denoted as NO2_c) were made with a Cranox instrument (Ecophysics, Switzerland) using a chemiluminescence detectors (CLD 770 AL). NO_2 was measured as NO after photolytic conversion (PLC 760). NO_2 measurements with molybdenum converter (denoted as NO2_m) were made using instruments from Horiba, Monitor Labs and TEI. Simultaneous NO_2 measurements with both converter techniques are available from January 1995 to August 2001 at Taenikon and are still ongoing since November 2001 at Rigi.
PAN measurements with gas chromatography and an electron capture detector (HP 5890A) were performed at Taenikon from April 1995 to November 1996.

Results

Fig. 1 shows a case study of a fair weather period for Taenikon 1998 that illustrates the increasing NO2_m to NO2_c difference (delta_NO2) with proceeding fair weather when more and more photochemically produced interfering compounds are present.
The molybdenum converter instrument overestimates the NO_2 most in the afternoon corroborated by high delta_NO2 and in particular low NO2_c / NO2_m ratios. The mean daily cycle of PAN for July and August at Taenikon (Fig. 2) demonstrates that at least a considerable part of the difference and of the daily variability can be explained by the PAN interference. Because HNO_3 is known for losses and memory effects in the inlet system, the difference of about 1ppb at the beginning of the fair weather period and the general increase of delta_NO2 can be likely attributed to nitric acid .

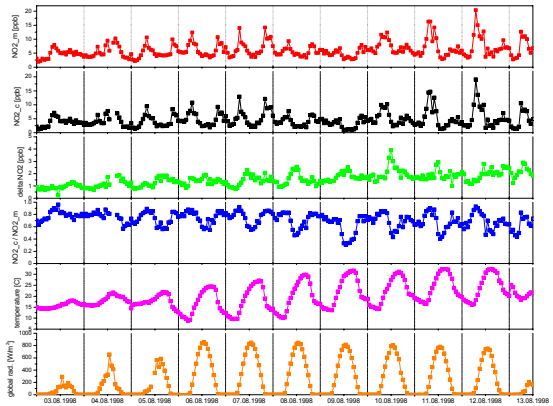

Fig. 1: Case study illustrating the diverging NO_2 signals for a clear weather period at Taenikon in August 1998.

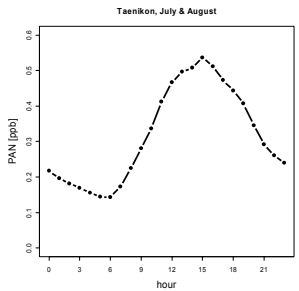

Fig. 2: Mean daily cycle of PAN for July and August at Taenikon.

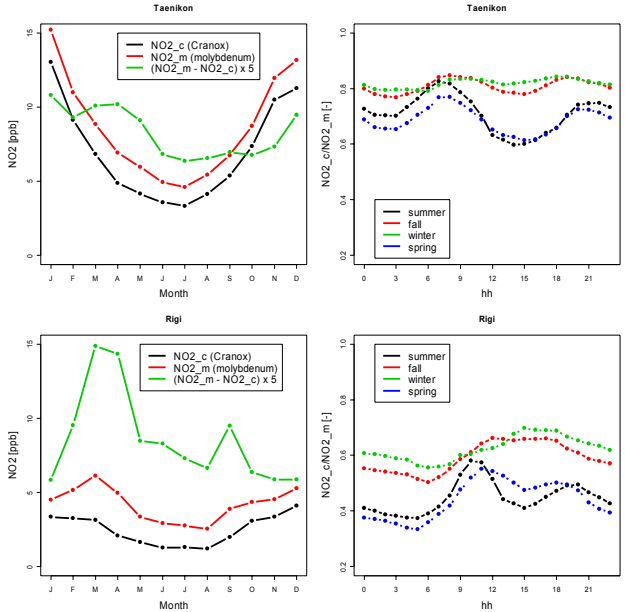

Fig. 3: left) Annual cycles of NO_2 measured with molybdenum and photolytic converter and their differences for Taenikon and Rigi. Differences are multiplied by 5. right) Daily cycles of the NO2_c to NO2_m ratio for each season for both sites.

Looking at annual cycles (Fig. 3), the delta_NO2 at Taenikon is highest in winter (when NO_2 concentrations are highest) and spring and peaks at Rigi in spring. The phenomenon in spring is similar to the frequently observed spring O_3 maxima at elevated sites that are most likely of photochemical origin [2].
On a relative scale, the NO2_m overestimates the NO_2 concentrations most during spring/summer due to higher solar input and more prevalent photochemistry. Then, the NO2_c to NO2_m ratio also shows a diurnal cycle with highest ratios in the morning when fresh emissions are measured and lowest ratios in the afternoon when the air masses are more photochemically aged. At Rigi, the morning peak appears later when the up-valley wind reaches the sampling site. During the night when residual layer air is measured, a NO2_c to NO2_m ratio of only 0.4 is observed.

Outlook

The differences of the NO_2 concentrations will be quantified for 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.

References

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[2] Brönnimann, *Phys. Chem. Earth* (C) 24 (5), 531-536, 1999.

Acknowledgements This research was financially supported by the Swiss Agency for the Environment, Forests and Landscape (SAEFL).

Contact: martin.steinbacher@empa.ch