Investigation of Anthropogenic HCHO/NO_x-Ratios and Comparison of two different HCHO Measurement Techniques

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Introduction

For the evaluation of an emission model two field campaigns have been performed in the Augsburg area in March and in October 1998. As part of an integrated concept (Slemr et al., 2002) of ground-based and air-borne measurements as well as tracer experiments the long-term measurements were applied to characterize the composition of the city plume of Augsburg. For this purpose a mobile laboratory was placed 5 km downwind of Augsburg in Stätzling, equipped with analytical instruments for the measurement of NO, NO_2, NO_y, CO, C_2 C_{10}-hydrocarbons, HCHO, O_3 and meteorological parameters (Klemp et al., 2002, Mannschreck et al., 2002). In this presentation special emphasis is placed on the results of atmospheric HCHO concentrations, measured by two different measurement techniques in March 1998: Tunable Diode Laser Absorption Spectroscopy (TDLAS) and a commercial Hantzsch monitor.

Scientific approach

Characteristic emission ratios of HCHO and NO_x were derived from measured concentration ratios 5 km downwind of the city using appropriate filter criteria:

- Wind direction filter in order to separate the data from the city sector from the whole data set.
- Wind speed filter in order to avoid photochemical degradation processes during transport between source and receptor.
- Correlation analyses in order to separate the impact of Augsburg and that of "Background air masses" on the emission ratios.

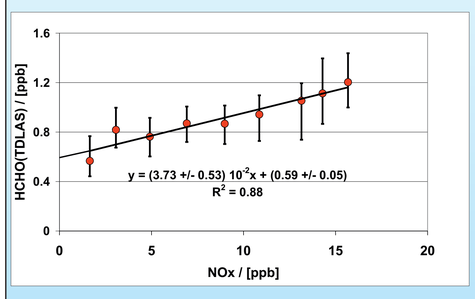
Measurement techniques

	Hantzsch	TDLAS
HCHO detection	Quantitative transfer of HCHO into the liquid phase and detection by fluorescence (exitation 400 nm, fluorescence: 510 nm of the Hantzsch reagent.	Detection via infrared-absorption of an single isolated absorption line at 1700 cm^{-1} using tunable lead salt lasers (linewidth $\lceil$ 10^{-4} cm^{-1}), a White cell of 100 m light path and 2-f-detection technique
Time resolution	3 min.	1 – 2 min.
Calibrations	Liquid standards	HCHO-permeation source
Detection limit	< 100 ppt	200 ppt
Precision at 1.5 ppb	15 %	15 %
Advantages of the method	Commercially availible Much easier to operate than TDLAS High sensitivity	High resolution spectroscopic technique Virtual immune to interferences Reference system against which other methods are often compared

Mean HCHO/NO_x-ratios

Problem: Abstraction from HCHO background fluctuations due to its water solubility

Different to NO_x, as a moderately soluble species, HCHO is substantially washed out by precipitation events. Whash-out of HCHO would influence the HCHO background concentrationes rather then cause losses during less than 30 minutes long transport between Augsburg and the receptor site. So, grouping of HCHO concentrations by classes of the co-emitted (Schmitz et al., 1999) and in first order non soluble NO_x will separate the meteorological influences from the HCHO/NO_x-emission ratios of Augsburg. Using this approach it is assumed that the mean HCHO concentrations calculated for the different NO_x classes consists of a mean HCHO background concentration and a NO_x-dependent HCHO term, which describes the HCHO/NO_x emission ratio of Augsburg.



Ambient air mixing ratios of HCHO were concurrently measured by TDLAS and by a commercial Hantzsch monitor during the EVA campaign (Klemp et al., 2002) in March 1998 as part of the German "Troposphärenforschungs-programm". Mean formaldehyde concentrations (based upon 10-minutes averages) for different NO_x-classes (ΔNO_x = 2 ppb). The error bars indicate the 25- and 75-percentiles of formaldehyde for each NO_x-class. The mean slope and ist 1-σ-standard deviations as well as R^2 are calculated by orthonormal regression analyses.

	HCHO/NO_x (ppb/ppb)	HCHO-Background (NO_x=1 ppb) (ppb)
AL4	$(3.28 \pm 0.48) \cdot 10^{-2}$ R^2 =0.82	0.49 ±0.07
TDL	$(3.73 \pm 0.53) \cdot 10^{-2}$ R^2 =0.88	0.61 ±0.05
Emission model	$3.3 \cdot 10^{-2}$	- -

Comparison of experimentally derived HCHO/NO_x-ratios with those from the emission model, provided by Institut für Energiewirtschaft und Rationelle Energieanwendung (IER), Universität Stuttgart (Kühlwein et al., 2002) for the March campaign.

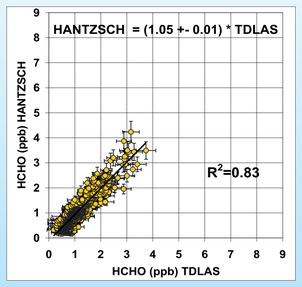
Results:

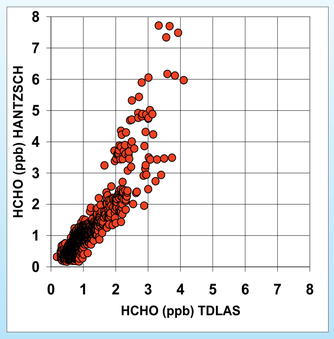
- Both, the HCHO/NO_x-ratios and the HCHO background concentrations are in good agreement for the two independent measurement techniques.
- Within their error limits, experimentally derived HCHO/NO_x-ratios agree with those from the emission model.

Comparison of concurrently measured HCHO-ratios

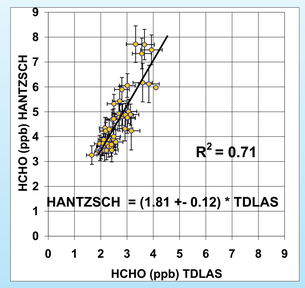
All data, Augsburg sector, Wind speed > 0.5 m/s

NO_y/NO_x < 1.25 and NO_y < 20 ppb





NO_y/NO_x > 1.25 and NO_y > 20 ppb



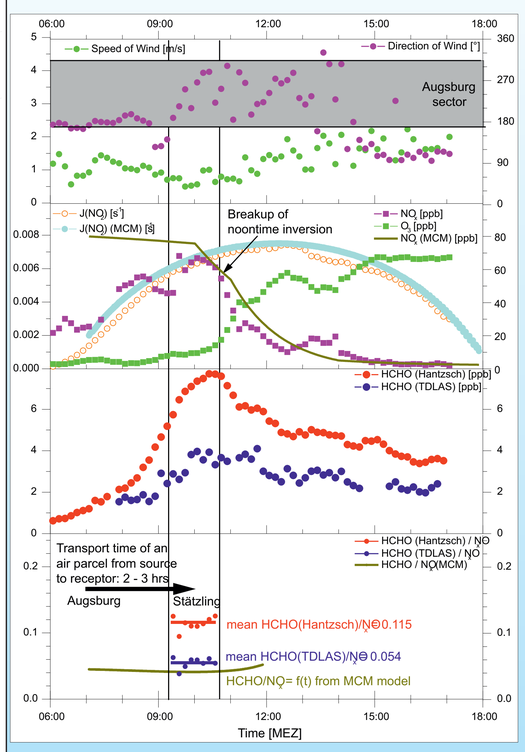
In order to study the effect of longer transport times from the city to the receptor place, the wind speed limit is set to 0.5 m/s. More than 1000 concurrently measured 10-min-averages are plotted.

Results:

- In most cases (i.e. HCHO < 2.5 ppb) good correlations are observed between Hantzsch and TDLAS.
- For high precursor concentrations and for sunny periods, which occured in the last few days of the campaign, we found deviations of up to a factor of 2. The Hantzsch method yields mixing ratios of up to 8 ppb whereas the TDLAS shows only values of around 4 ppb. Using NO_y > 20 ppb and NO_y/NO_x > 1.25 as discrimination levels both scenarios can be separated successfully.
- It has to be noted, that HCHO mixing ratios of up to 8 ppb are observed independently by two different Hantzsch systems during an ambient air intercomparison at the end of the campaign.

Box model study

For a period of summer smog (31. 3. 1998, last day of the EVA-1 campaign) with substantial deviations between both techniques, a box model study was performed using the MCM model (Derwent et al., 1998). Such a box model study leads to reasonable results as long as exchange of polluted air masses from Augsburg with those from the free troposphere is hindered by a stable inversion layer during the morning hours.



Air masses from Augsburg are advected to Stätzling from the early morning hours up to 14:00 with low wind speeds of (1.0 +- 0.5) m/s.

The day is characterized by clear-sky-conditions. The break-up of the inversion layer took place at 10:45, c.f. crossing of the plotted O_3- and NO_x-lines. Dilution was adjusted in a way that modeled NO_x-values (start: 80 ppb at 7:00) follow the temporal behaviour of measured values.

HCHO concentrations measured by the Hantzsch system and by TDLAS both show highest levels at around 10:00, as is also observed for NO_x, but Hantzsch levels were up to twice as high as the ones measured by the TDLAS system.

Modeled HCHO/NO_x-ratios can be compared with HCHO(TDLAS)/NO_x-ratios and HCHO(Hantzsch)/NO_x-ratios only between 9:15 (minimal transport time, cf. wind speed) and 10:45 (break-up of inversion layer). Modelled and measured ratios deviate by more than a factor of 2 in case of the Hantzsch measurement, whereas the TDLAS ratios are close together with the modeled ratios. The scatter of the individual datapoints shows that the differences between both ratios are significant.

Boundary conditions for the MCM box model run:

HC/ NO_x = 2.5 ppbC/ppb
HCHO/NO_x = 0.035 ppb/ppb
HCHO- background concentration = 0.8 ppb
45 individual Hydrocarbons were considered.

Mixing height below the persistent inversion layer: 300 m
$K_{Dep}(NO_2)$ = 0.25 cm/s
K_{Dep}(HCHO) = 0.5 cm/s

Results

- Wind speed, wind direction and the existence of a stable inversion layer guarantee that the air measured in Stätzling between 9:15 and 10:45 originates from Augsburg.
- Using the results of our long-term measurements as starting conditions, the MCM-model run yields a HCHO/NO_x mixing ratio between 0.04 and 0.05.
- This is in good agreement with the value obtained by the TDLAS (mean: 0.054) and far from the mixing-ratios

Conclusions

- An agreement of better than 10 % between Hantzsch and TDLAS is observed for low and moderately polluted conditions.
- Within their error limits, experimentally derived HCHO/NOx-ratios agree with those derived from the emission model provided by IER.
- For heavily polluted events under photochemically active conditions the Hantzsch system shows higher values of up to a factor of two.
- The reasons for this behaviour are still unknown, but there are two arguments which suggest that the Hantzsch HCHO levels are biased by an interference under those conditions:

==> The observed $HCHO^{Hantzsch}/NO_y$-ratios yield values of up to 11%, whereas the $HCHO^{TDLAS}/NO_y$-ratios stay constant at around 4% (as it is observed as average throughout both EVA-campaigns).

==> Additional production of HCHO from photochemistry can be excluded from a box model study to be the reason for differences of up to 4 ppb during transport from the city to the receptor place (5 km downwind).

References

Derwent, R. G., M. E. Jenkin, S. M. Saunders, and M. J. Pilling, 1998. *Atmos. Environment*, **32**, 2429 - 2441.
Klemp, D., K. Mannschreck, H.W. Pätz, M. Habram, P. Matuska, F. Slemr, 2002. *Atmos. Environment*, in press.
Kühlwein, J., B. Wickert, A. Trukenmöller, R. Friedrich, J. Theloke, 2002. Atmos. Environment, in press
Mannschreck, K., D. Klemp, D. Kley, R. Friedrich, J. Kühlwein, B. Wickert, P. Matuska, M. Habram, F. Slemr, 2002. *Atmos. Environment*, in press.
Schmitz, Th., D. Hassel and F.J. Weber, 1999. *Jül.-3646.*
Slemr, F., G. Baumbach, P. Blank, U. Corsmeier, F. Fiedler, R. Friedrich, M. Habram, N. Kalthoff, D. Klemp, J. Kühlwein, K. Mannschreck, M. Möllmann-Coers, K. Nester, H.J. Panitz, P. Rabl, J. Slemr, U. Vogt, B. Wickert, 2002. *J. Atmos. Chemistry,* in press.