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UPDATE OF THE ROMBERG-APPROACH AND SIMPLIFIED NO / NO$_2$ CONVERSION MODEL UNDER CONSIDERATION OF DIRECT NO$_2$-EMISSIONS

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Abstract: Although many German monitoring sites report declines of NO$_x$-concentrations, NO$_2$-concentrations actually stagnate or even increase quite often. Various analyses have identified the altered compositions of nitrogen oxides (NO$_2$/NO$_x$-ratio) emitted by motor vehicles (resulting in an increase of primary NO$_2$-emissions) as well as the chemical environmental conditions (mainly ground level ozone) as the main cause. The chemical conversion of NO to NO$_2$ is often parameterized in dispersion calculations of exhaust emissions. A widely applied conversion model is the so-called Romberg approach from 1996. However, the Romberg approach has to be re-evaluated to accommodate the above-mentioned conditions. This article presents an adjustment to the Romberg approach in accordance with the measured data from 2000 to 2006, taking into consideration substantially higher NO/NO$_2$-conversion rates especially for higher NO$_x$-concentrations. Model calculations with OSPM (Operational Street Pollution Model) including its internal chemistry module are able to reproduce very well the trends in the measured annual NO$_2$-concentrations over a 10 year period. The relevant parameters for variations between the years are the NO$_x$-emissions, primary NO$_2$-emissions, ozone concentrations, wind conditions, and background concentrations. A simplified chemistry model based on annual mean NO$_x$- and NO$_2$-concentrations, and background ozone concentrations, as well as primary NO$_2$-emissions is presented as an alternative to the updated Romberg approach. This model simulates the annual mean NO$_2$-concentrations much more accurately than the conventional and the updated Romberg approaches.

Key words: primary NO$_2$-emission, NO/NO$_2$-conversion rates, motor vehicles emission

INTRODUCTION
The formation of NO$_2$ from NO is a complex photochemical process. It is mainly depending on the total amount of available NO$_x$ and ozone. The ambient NO$_2$-concentration is also depending on the primarily emitted NO$_2$. Besides NO-emission, ozone concentrations as well as primary NO$_2$-emission are changing from year to year.

To date, the empirical conversion model of Romberg *et al.* (1996) is often used for dispersion calculations. It describes the conversion according to a [NO$_2$] = f ([NO$_x$]) equation with

$$[NO_2] = \frac{A \cdot [NO_x]}{[NO_x] + B} + C \cdot [NO_x] \tag{1}$$

where A, B, and C are regression parameters. Two sets of parameters exist for both the annual average value as well as the 98-percentile value. The results of this model are satisfactory, however they cannot describe the tendency to stagnating or slightly increasing NO$_2$-concentrations, which has been observed by data from roadside monitoring stations over the last years (Bächlin *et al.*, 2006). This is due to changes in ozone values compared to before 1996, when the model was calibrated, as well as increased primary NO$_2$-emissions following increases in installations of after-treatment systems in automobile exhausts (Oxidation catalysts).

UPDATING THE ROMBERG APPROACH
Romberg *et al.*'s (1996) approach was recalibrated to current data within a research project for the regional environmental office of North Rhine-Westphalia. Based on the approach described above (equation 1), the coefficients for A, B, and C were determined according to the new data sets. They were adjusted to capture the annual average values, the 98-percentile values, and the 19th-highest hourly values. The data were evaluated for the years 2004, 2005, and 2006 in Bächlin and Bösinger (2008) accordingly to Romberg *et al.* (1996) and graphically displayed. The regression functions were computed by using the least square method.

The constants for equation 1 are listed in Table 1 for the given period of 2004 to 2006 along with the parameters from the conventional approach. Figure 1 shows the observed NO$_2$-concentrations depending on NO$_x$, as well as the two regression curves. Next to the values for the conventional method the new regression results are plotted together with the observed data. The regression parameters match those in Tab. 1. It can be clearly seen that the approach by Romberg *et al.* (1996) results in too low NO$_2$-values for high NO$_x$-values. According to the earlier (1996) approach, a NO$_x$-value of approx. 81 µg NO$_x$/m^3 yielded a NO$_2$-value around the limit of 40 µg/m^3. Using the updated approach, slightly lower NO$_2$/NO$_x$-ratios are predicted in this range. The annual average value of 40 µg NO$_2$/m^3 would be reached by an annual mean NO$_x$-concentration of approx. 88 µg/m^3 with the new approach.

Table1: Parameters for the regression of NO_2/NO_x ratios according to equation (1) (Bächlin and Bösinger, 2008). Units for NO_2 and NO_x concentrations are in μg $(NO_2)/m^3$.

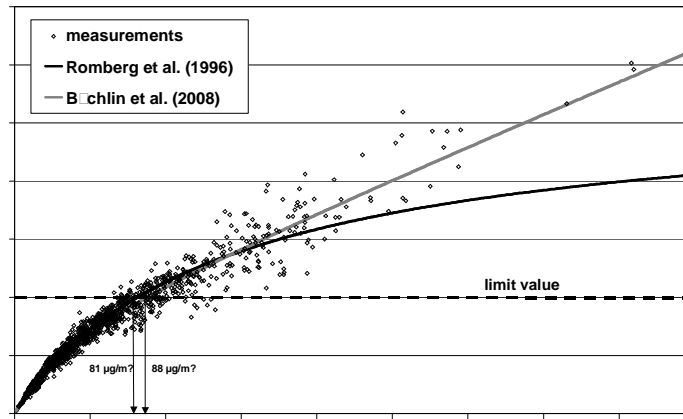| Statistical concentration parameters	parameter of function		
Romberg et al. (1996)	**A**	**B**	**C**
annual average	103	130	0.005
98-percentile	111	119	0.039
B chlin et al. (2008)	**A**	**B**	**C**
annual average	29	35	0.217
98-percentile	40	20	0.170
19. highest hourly value	43	10	0.151

Figure 1: Measured annual mean NO_2-concentrations as a function of NO_x, and both regression curves. Source: Bächlin and Bösinger (2008)

OSPM CHEMISTRY MODEL

More realistic conversions can be obtained if a chemistry model is applied. A simplified relation is often used to describe the chemical conversion in the equilibrium state of NO_2, NO, and ozone. The assumptions leading to the simplifications are:

- An equilibrium in the system NO_2-NO-O_3 is quickly obtained
- The reaction with volatile organic compounds (VOC) is not considered
- Mixing processes and sinks (advection, turbulent diffusion, influence of boundary conditions, deposition) are parameterized via the mixing time
- The contribution of traffic emissions is estimated by the difference of the measured NOx-concentration at two air quality monitoring sites or calculated via a dispersion model
- The influence of the wind direction is not considered.

The considered reactions are:

$$NO + O_3 \Rightarrow \quad NO_2 + O_2 \qquad (k) \qquad\qquad (2)$$
$$NO_2 \Rightarrow \quad NO + O_3 \qquad (J) \qquad\qquad (3)$$

J (s^{-1}) is the photolytic frequency of NO_2, k $(ppb^{-1} s^{-1})$ is the reaction coefficient.

Assuming that the equilibrium is quickly reached, the differential equations turn into three algebraic conditional equations. Solving them yields the analytical equation for the concentration:

$$[NO_2] = 0.5 \left(B - \sqrt{B^2 - 4 \left([NO_x] \, [NO_2]_O + [NO_2]_n / k\tau \right)} \right) \qquad\qquad (4)$$

With the variables

$$[NO_2]_n = [NO_2]_V + [NO_2]_B \qquad\qquad [NO_2]_O = [NO_2]_n + [O_3]_B \qquad B = [NO_x] + [NO_2]_O + \frac{1}{k}\left(J + \frac{1}{\tau} \right)$$

The two terms $[NO]_V$ and $[NO_2]_V$ are the amount being produced by traffic emissions as an increase of concentration above the background concentration. $[NO_x]_V$ is calculated from the difference in NO_x between the traffic station and the background station as

$$[NO_2]_V = p \left([NO_x] - [NO_x]_B \right) \qquad\qquad (5)$$
$$[NO]_V = \left([NO] - [NO]_B \right) \qquad\qquad (6)$$

with p = NO_2/NO_x being the fraction of NO_2 in the direct traffic emissions and $[NO_x]$ the concentration, which is estimated at the traffic station by measurements or dispersion model. This equation is used in the dispersion model OSPM to calculate the

NO_2 conversion within an hourly resolution (Palmgren *et al.*, 2007; Berkowicz, 2000). The parameter τ is calculated by meteorological values (e.g. wind speed and turbulence) as well as the road geometry (height of the street canyon) and represents the typical residence time the pollution is trapped inside the street canyon and is available for chemical reactions (see Berkowicz *et al.*, 1997). Typical values for τ are in the range of 80s to 150s.

The average hourly NO_2-values calculated via the OSPM chemistry model (considering hourly data of primary NO_2 emissions, ozone concentrations, global radiations, temperature, and wind speed) match the observed data in 2006 from the station Corneliusstraße in Düsseldorf (see Figure 2) very well. Comparable results have been optained at other stations and for other years. Therefore, the OSPM chemistry model is well suited to describe the formation of NO_2, while considering the relevant influences in the NO-NO_2-O_3 cycle, including the primary NO_2-emissions.
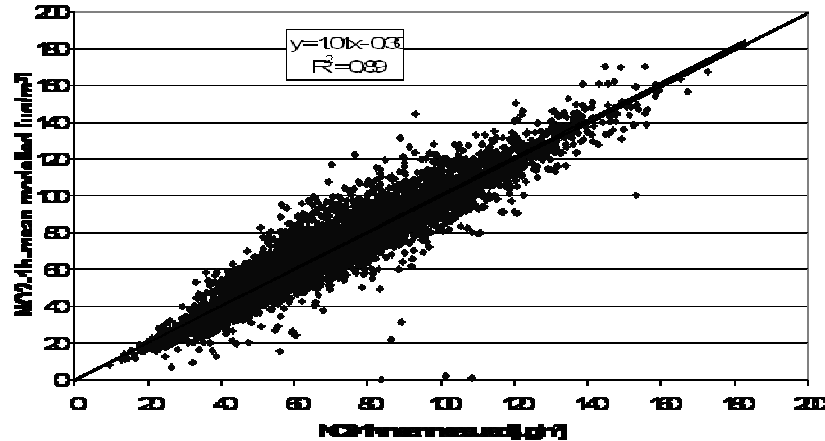

Figure 2: Comparison of hourly mean NO_2-concentrations, calculated with the OSPM chemistry model from observed NO_x data, and values from the measurement site Corneliusstraße in Duesseldorf for the year 2006.

SIMPLIFIED CHEMISTRY MODEL BASED ON ANNUAL AVERAGE VALUES

Strictly speaking, the above equations of the chemistry model can only be used in time series calculations, because the parameters J and k are dependent on meteorological parameters. However, based on research projects by BASt (Bundesanstalt für Straßenwesen) (Düring *et al.*, 2009a) as well as the Landesumweltamt Brandenburg (Düring and Bächlin, 2009b), these equations can also be applied for annual mean concentrations using the following parameters:

J $= 0.0045 \ s^{-1}$
k $= 0.00039 \ m^3 \ (ppb \ s)^{-1}$
τ = 100 s (street canyons) or 40 s (free dispersion)

The input data is the same as for the Romberg approach:

   NO_x- annual mean at traffic station (observed value or estimated by dispersion model)
   NO_x- annual mean at background station
   NO_2- annual mean at background station
as well as two additional values:
   Ozone- annual mean at background station
   p = share of primary NO_2 emissions for all NO_x emissions.

The conversion calculations were performed with these values for observation data along rural and city roads. The NO_x concentration, the background NO_2-concentration, and the ozone concentration were set as annual average values for each individual traffic station and the corresponding representative background station. The results are given in Figure 3 for monitoring sites along federal highways. Figure 4 shows the data from a city road as an example.

CONCLUSIONS

The following can be observed:
- The approach by Romberg *et al.* (1996) is often conservative for existing data up to the year 2003; however, it cannot reproduce the long term trends (e.g. A4_1k and A4_2k in Figure 3).
- The approach by Bächlin and Bösinger (2008) reproduces the existing measured data better than the approach by Romberg, but it cannot reproduce the long term tendencies very well, either (Figure 3 and Figure 4).
- The simplified chemistry model that was introduced here can best reproduce the tendencies and the absolute values.
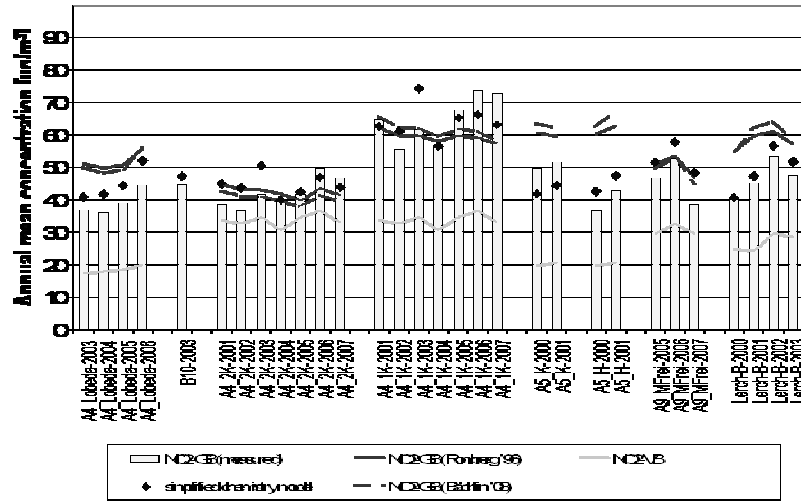
Figure 3: Annual mean NO$_2$-concentration from federal highway measurement sites, including values estimated from different conversion models. VB = background concentration; GB = total concentration
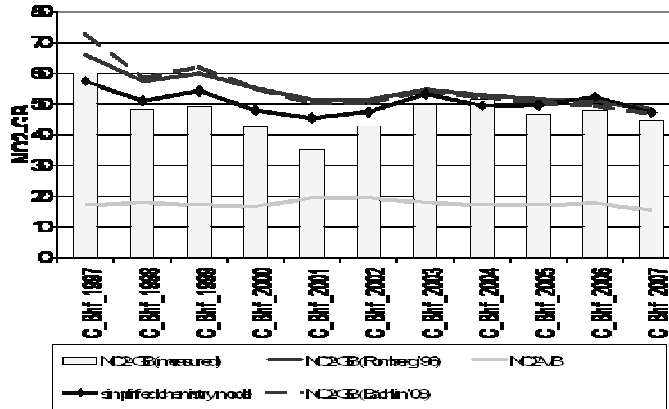

Figure 4: Annual mean NO$_2$-concentration in µg/m³ from the measurement site Bahnhofstraße (Cottbus), including values estimated from different conversion models. VB = background concentration; GB = total concentration

The main reason for the good fit for trends in the NO$_2$/NO$_x$ ratios is the explicit incorporation of the share of primary NO$_2$ emissions. Figure 5 shows the annual mean NO$_2$-concentration depending on the annual mean NO$_x$-concentration for the simplified chemistry model at a share of 6%, 16% and 25% primary NO$_2$ share assuming typical background values for ozone and NO$_2$, as well as the parameterization by Romberg et al. (1996) and Bächlin and Bösinger (2008), for comparison. It can be seen that the Romberg-parameterization matches with the curve for p=6%. This was expected since the calibration was performed before 1996 and p was about 5% to 10% at that time. The parameterization by Bächlin and Bösinger (2008) can be reproduced with a p of 16%. The calibration for this model was done on data from 2003 to 2006, and the average NO$_2$ emission share then was between 12% and 17%.
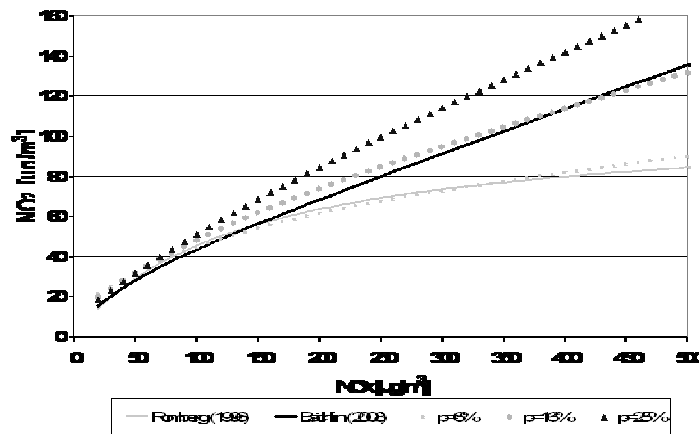

Figure 5: Dependence of annual mean NO$_2$- on annual mean NO$_x$-concentration, estimated with different models.

A further increase of NO_2 shares is to be expected over the next years (e.g. IFEU, 2007) leading to a further increase of the NO_2/NO_x ratios. This also means: the higher the proportion of primary NO_2 emission becomes, the more NO_x emissions have to be reduced in order to comply with the limit value of 40µg/m³. Figure 6 shows the comparison between annual mean NO_2-values concentrations, calculated via the simplified chemical model, and measurements from more than 30 German monitoring sites (highways and city roads) between 1997 and 2006. It can be noted that this approach reproduces the observed data very well. The correlation coefficient is r²=0.88, the slope of the curve is approx. 1. Therefore, this model is better suited to calculate the NO-NO_2 conversion than the parameterization by Romberg *et al.* (1996) and Bächlin and Bösinger (2008), by explicitly including primary NO_2 emissions and ozone concentrations.
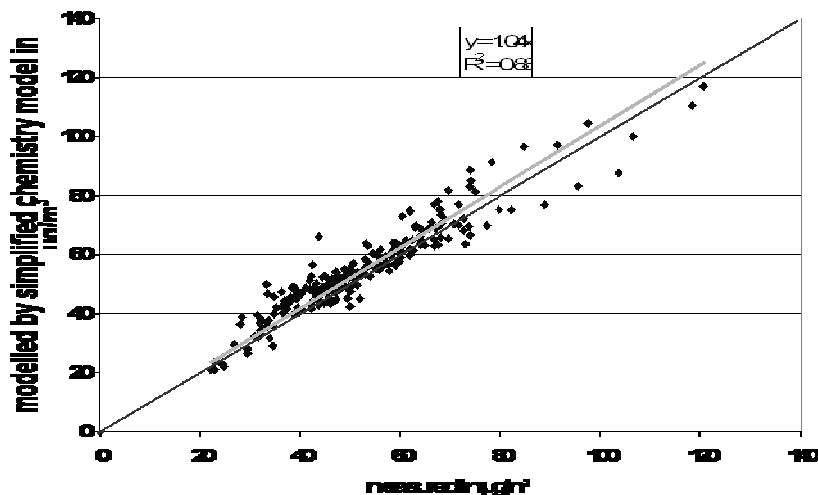

Figure 6: Comparison of results for annual mean NO_2-concentration with the simplified chemistry model and measurement data.

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