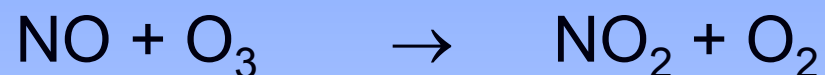


The urban „nitrogen dioxide (NO₂) problem“ Why is NO₂ not decreasing?

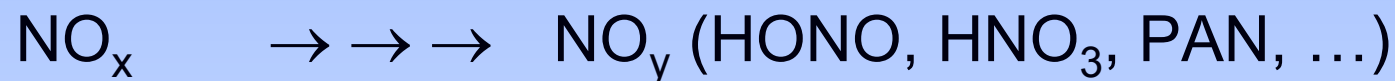
Jörg Kleffmann
Universität Wuppertal, Germany



- *Nitrogen oxides* (**NO_x**=NO+NO₂)
- NO_x mainly emitted as NO (ca. 80-95 %)
- NO₂ formed through the oxidation of NO in the atmosphere:



- Chemistry of NO_x leads to *reactive nitrogen species* (**NO_y**):

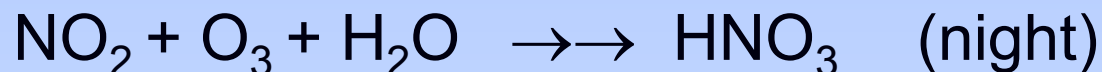
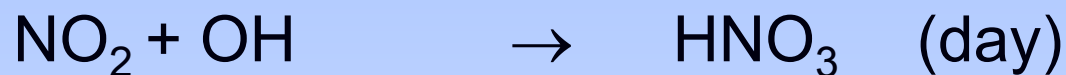


Def.: **NO_y** = Σ N/O-species (Ox.-state N ≥ 2)

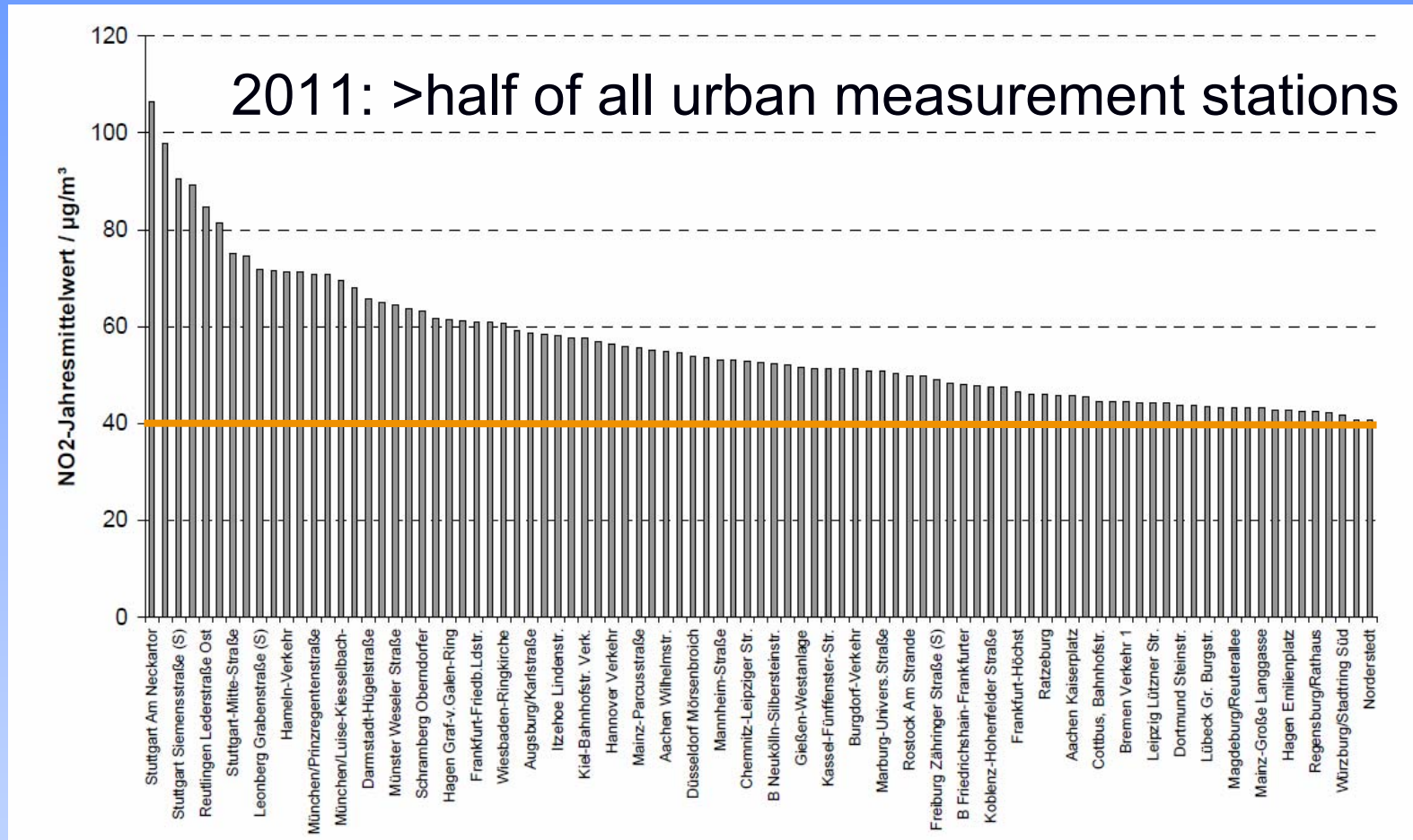
- NO_x important for ozone formation



- Oxidation of NO₂ and wet deposition leads to „acid rain”

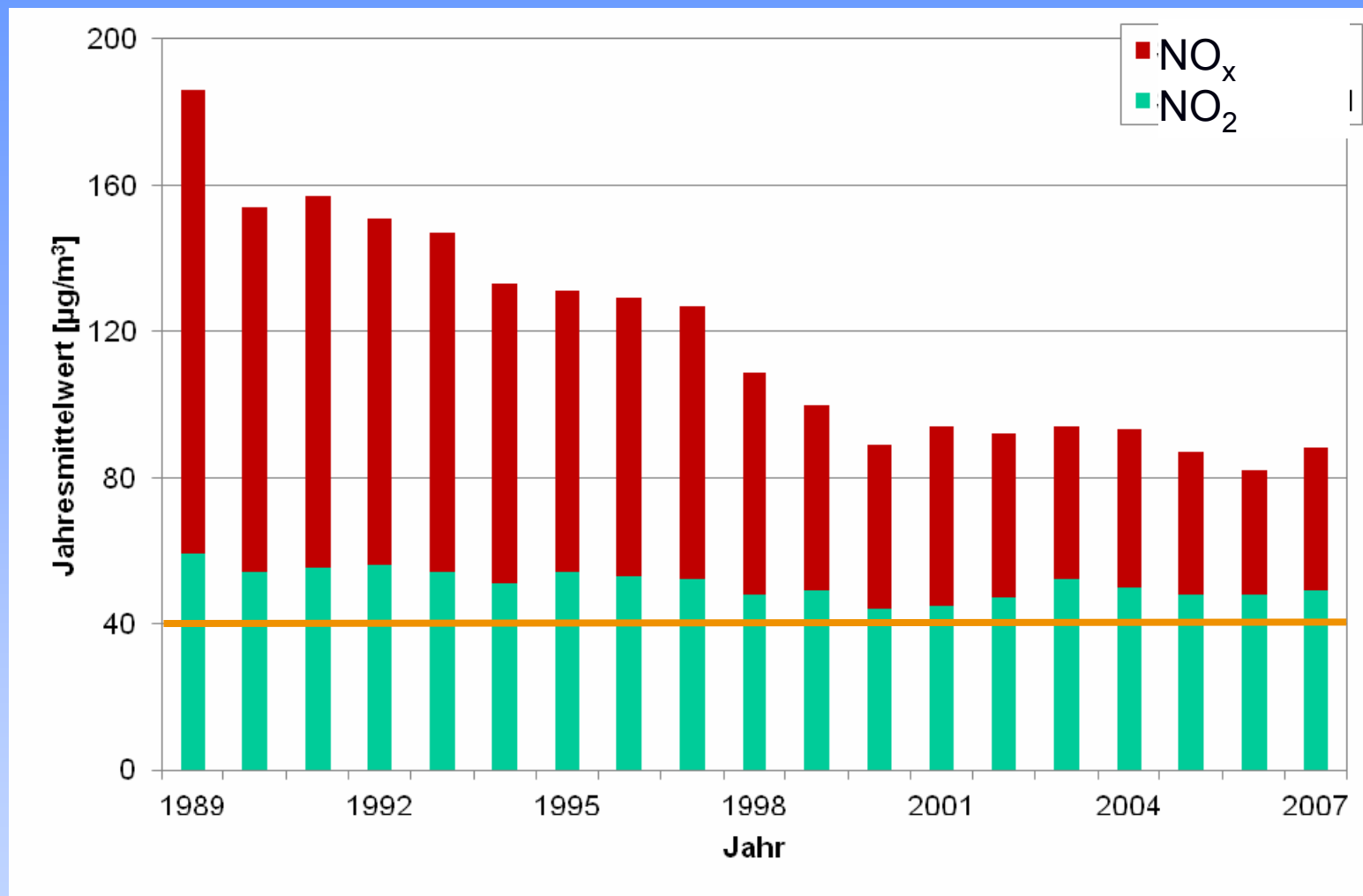


- NO₂ and reaction products (HONO, HNO₃, PAN,...)
directly harmful
- ➔ **NO₂**: from 2010 low EU-limit values (~20 ppb)
- Typical exceeded



German stations (2007), which exeed the limit for NO₂ of 40 µg m⁻³ (*Bruckmann, 2010*)

- NO_2 and reaction products (HONO, HNO_3 , PAN,...)
direly harmful
- ➔ **NO_2** : from 2010 low EU-limit value (~20 ppb)
- Typical exceded
- NO_x -reduction from combustion not successful
($\text{NO}_x \downarrow \text{NO}_2 \rightarrow$)



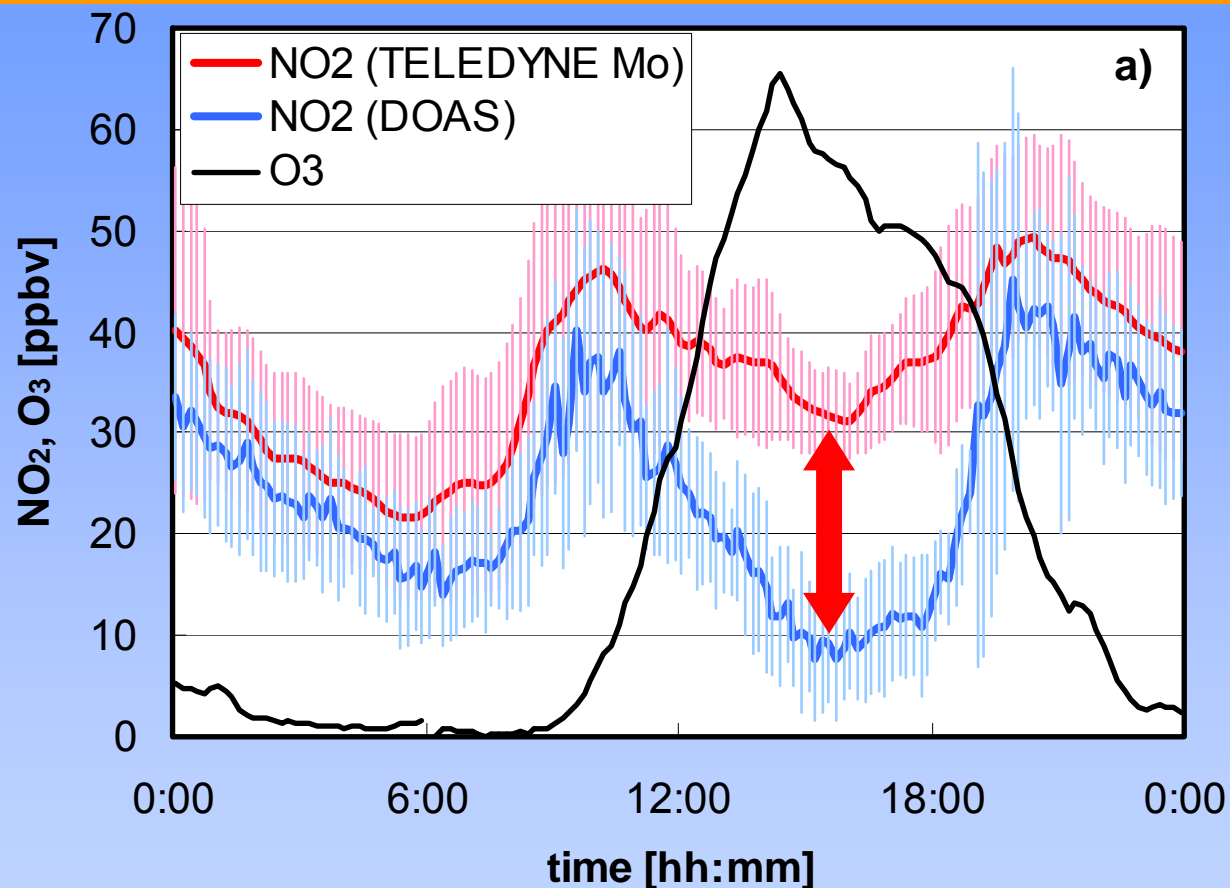
Urban measurement stations in NRW (LANUV, 2008)

- NO₂ and reaction products (HONO, HNO₃, PAN,...) direly harmful
- ➔ **NO₂**: from 2010 low EU-limit value (~20 ppb)
- Typical exceded
- NO_x-reduction from combustion not successful
(NO_x ↓ NO₂ ➔)
- What are the reasons for the stagnating NO₂ levels?
- Increasing direct emissions?
- Secondary formation in the atmosphere?

- Since 2004 emission measurements of NO, NO₂ and ozone (O₃) were carried out in the city of Wuppertal, close to main road (Friedrich-Engels-Allee).

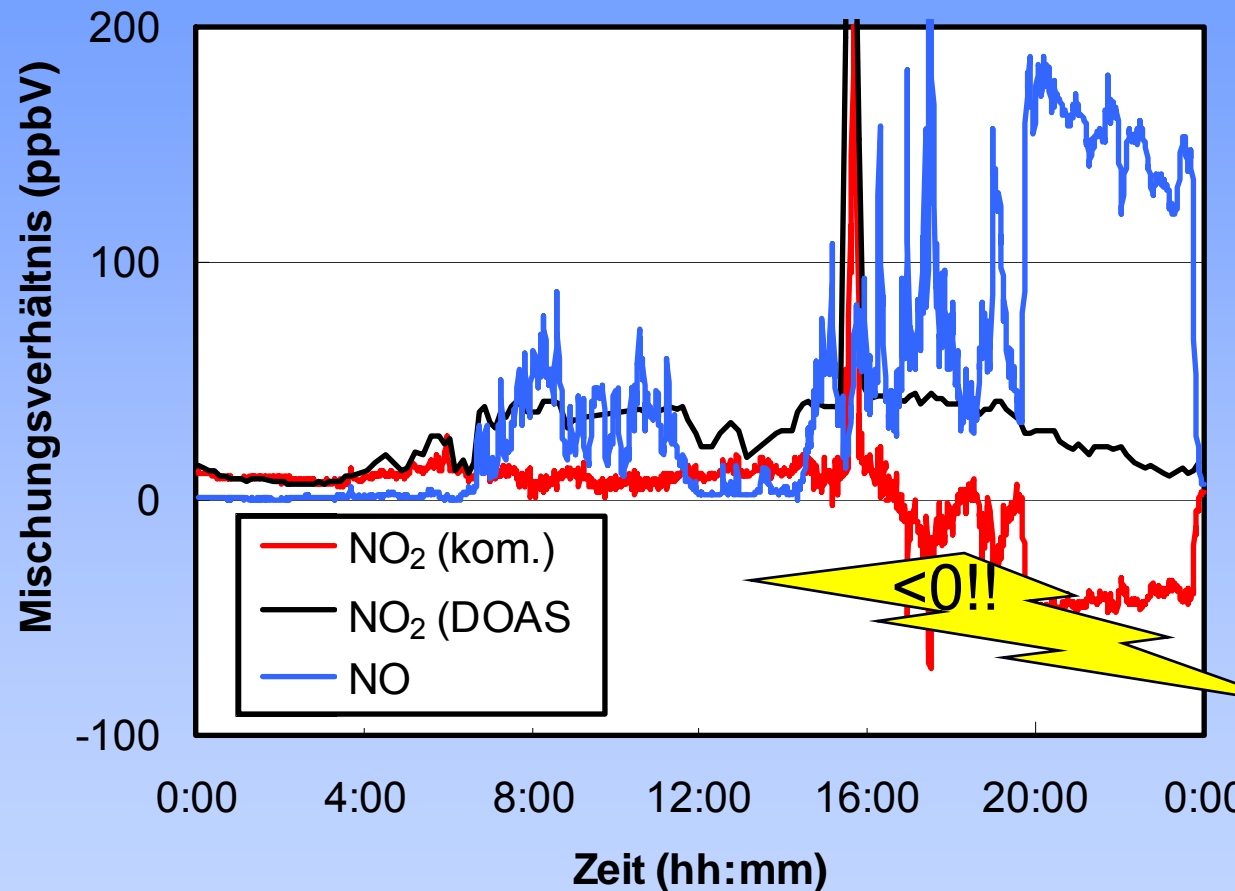


- Recommended standard instrumentation used
- O₃: UV-absorption
- NO_x: Chemiluminescence with Mo-converter...
- Known interferences...

NO₂ in Santiago de Chile (Chemiluminescence/Mo)

**Positive interferences by NO_y (PAN, HNO₃, Nitrate...)
→ Photolytic converters recommended...**

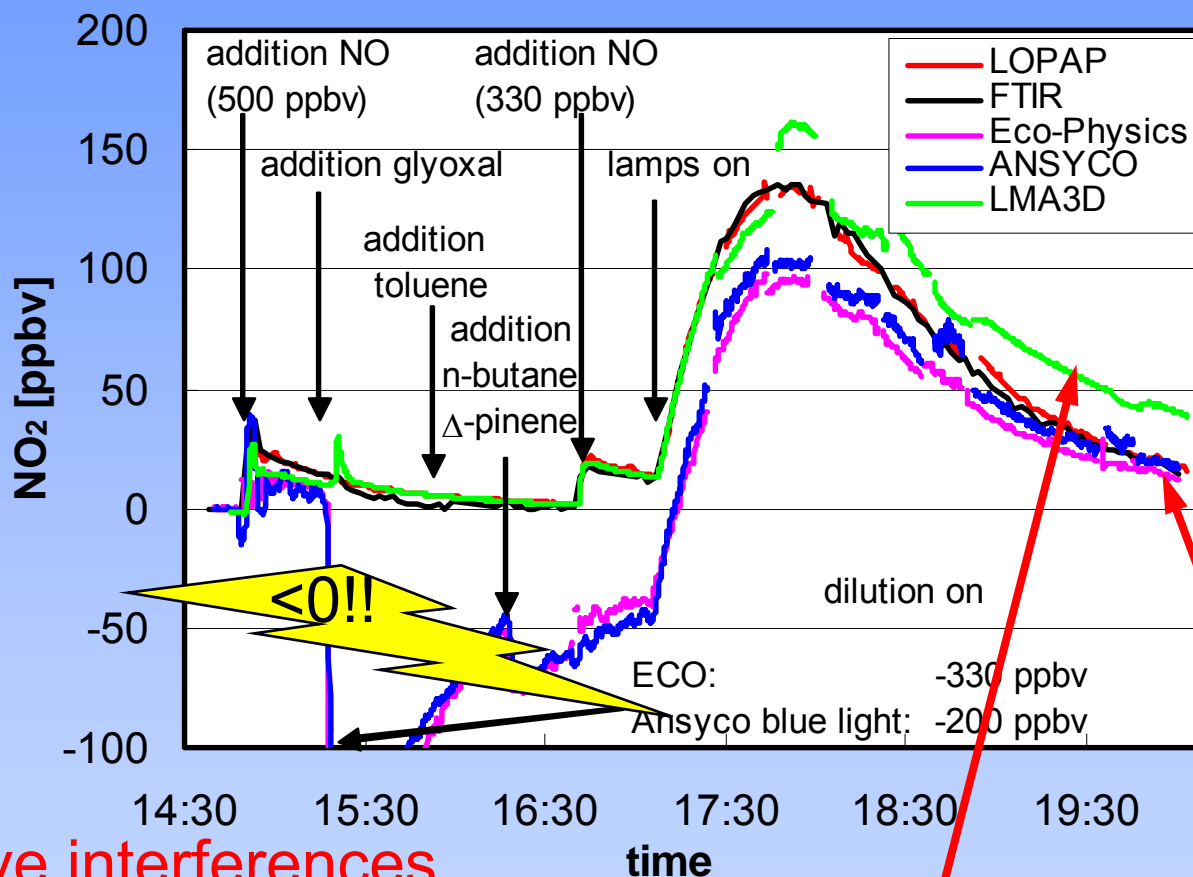
NO₂ in a tunnel (Chemiluminescence/photolysis)



Villena et al., 2012

Why negative NO₂?

NO₂ in a smog chamber (FTIR+Chemil.+ NO₂-LOPAP)



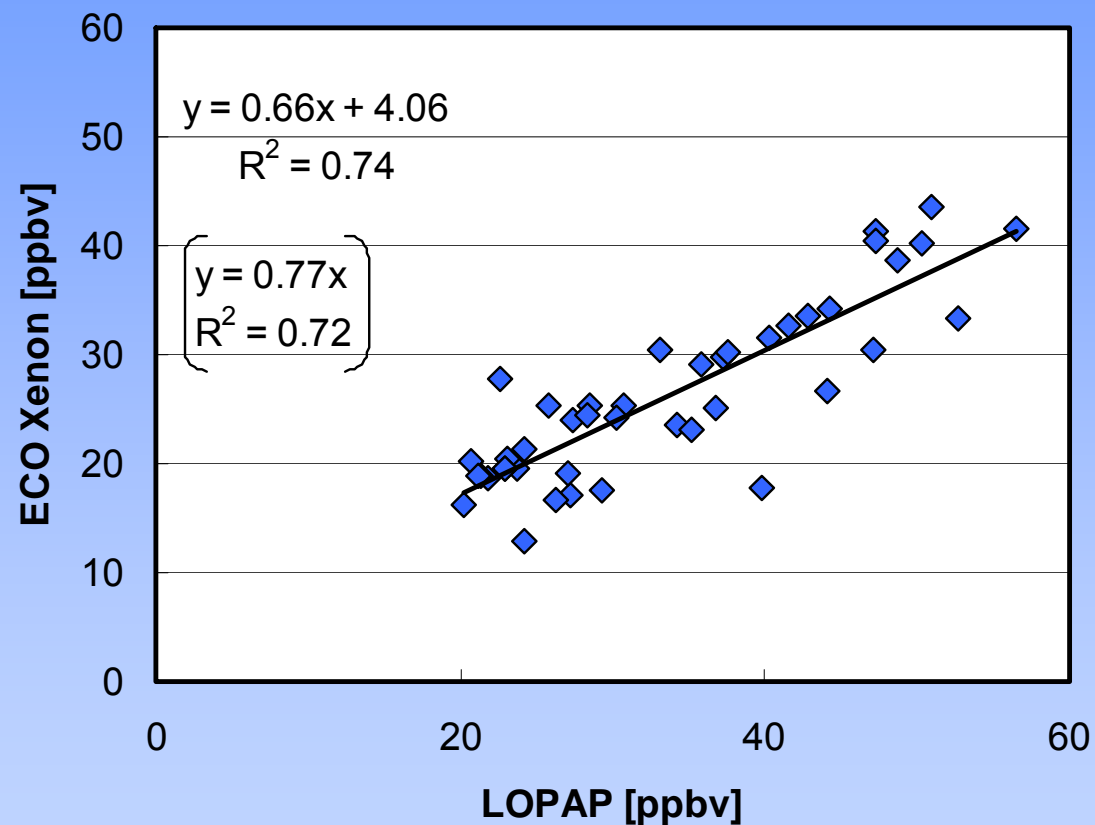
Negative interferences
by HO₂/RO₂ + NO

Positive interferences by PAN

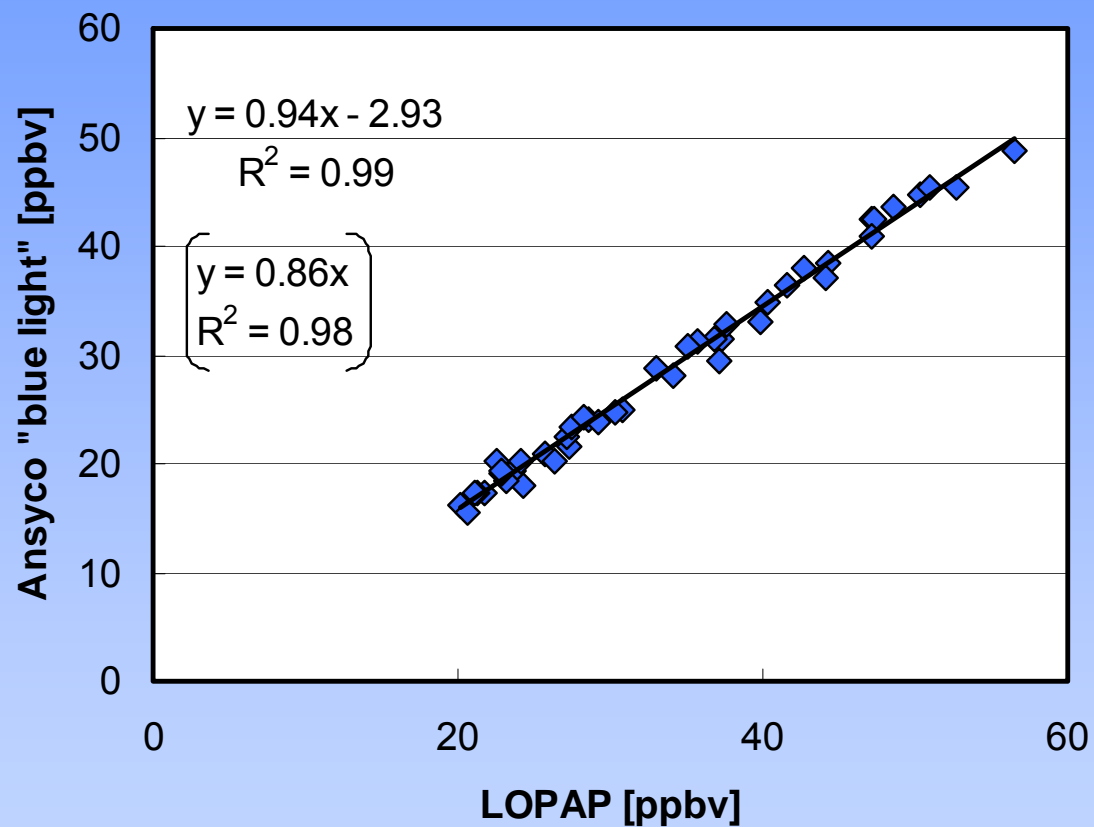
Successful intercomp. LOPAP/FTIR

Villena et al., 2012

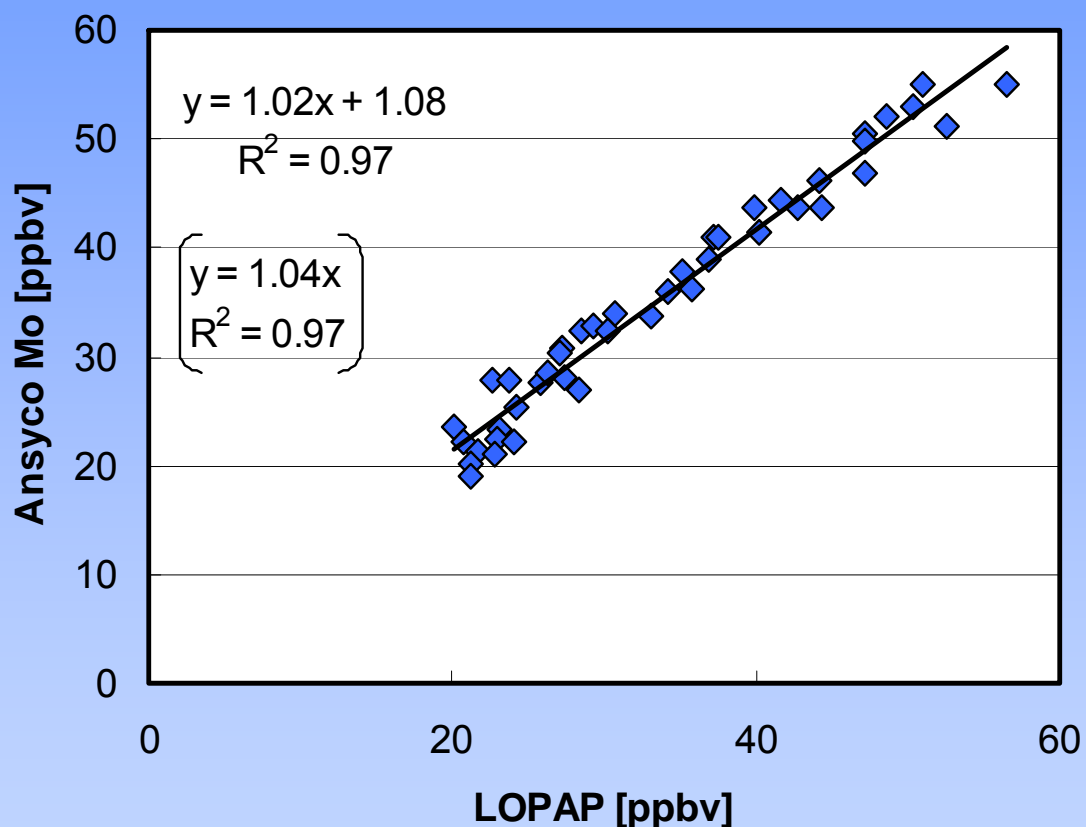
➤ NO₂-interferences at the B7, Wuppertal



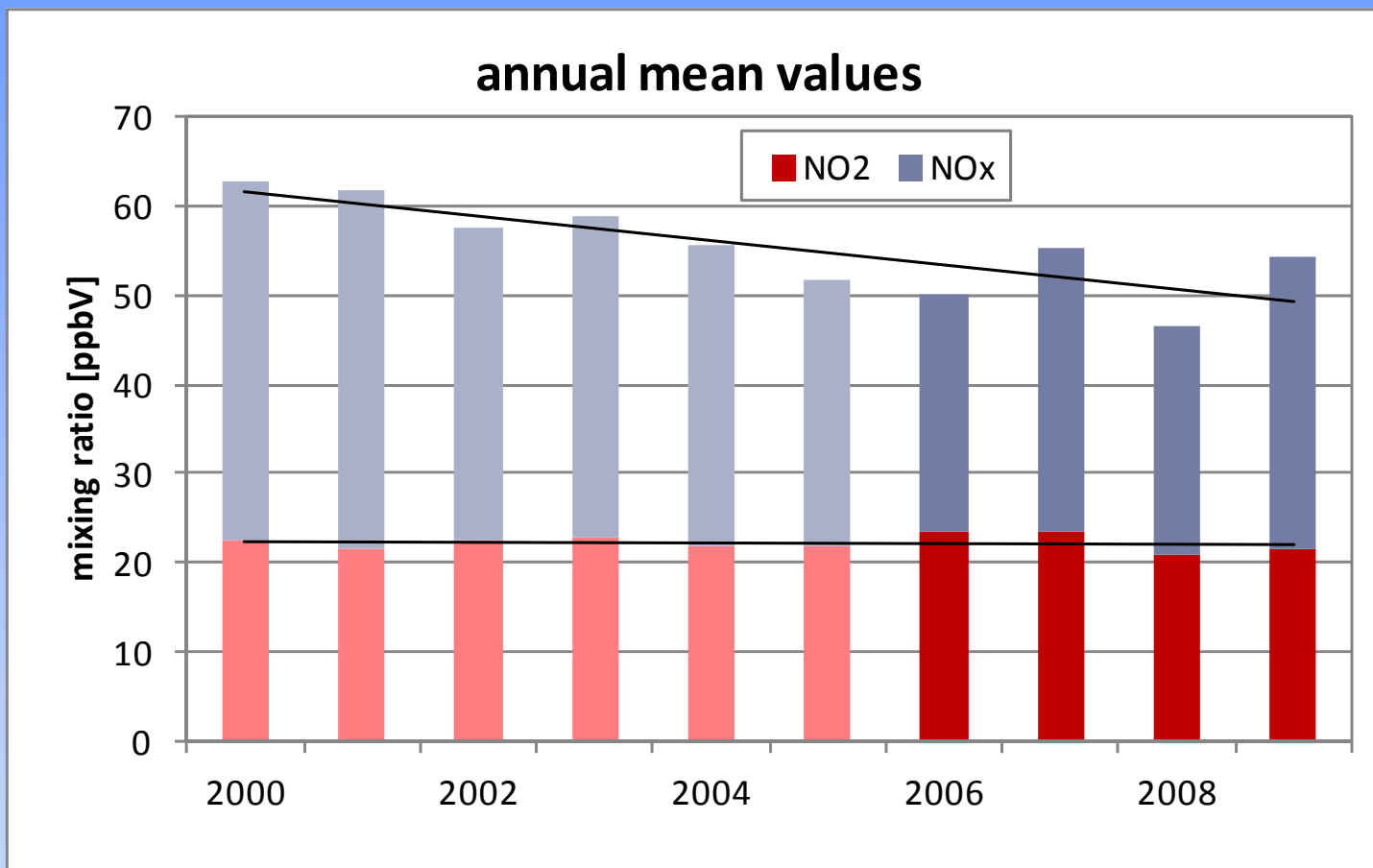
➤ NO₂-interferences at the B7, Wuppertal



➤ NO₂-interferences at the B7, Wuppertal

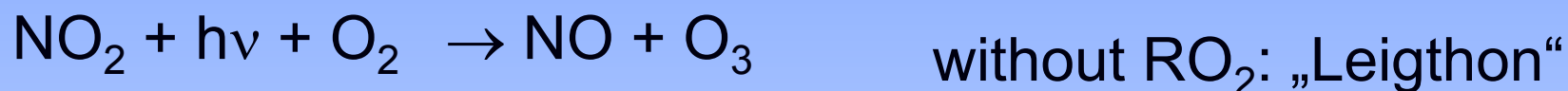
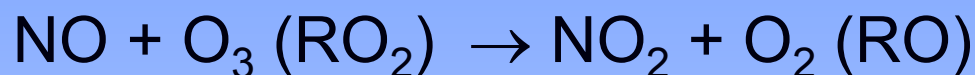


➔ Close to emission source: Mo-converters better than photolytic converters!



- Same NO_x and NO_2 trend was found.

- Determination of primary and secondary NO₂
- Direct measurement of primary NO₂ not possible
- NO₂ influenced by secondary formation:



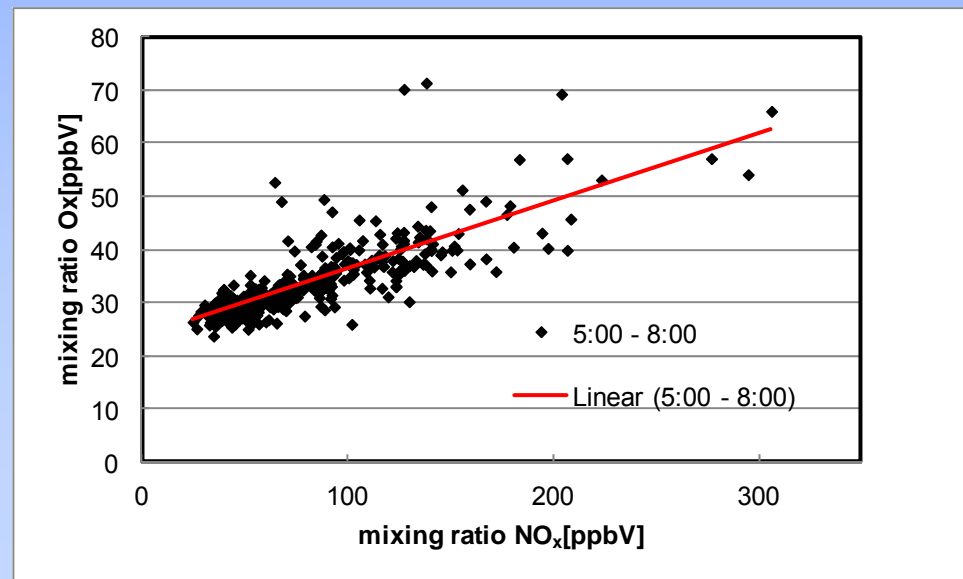
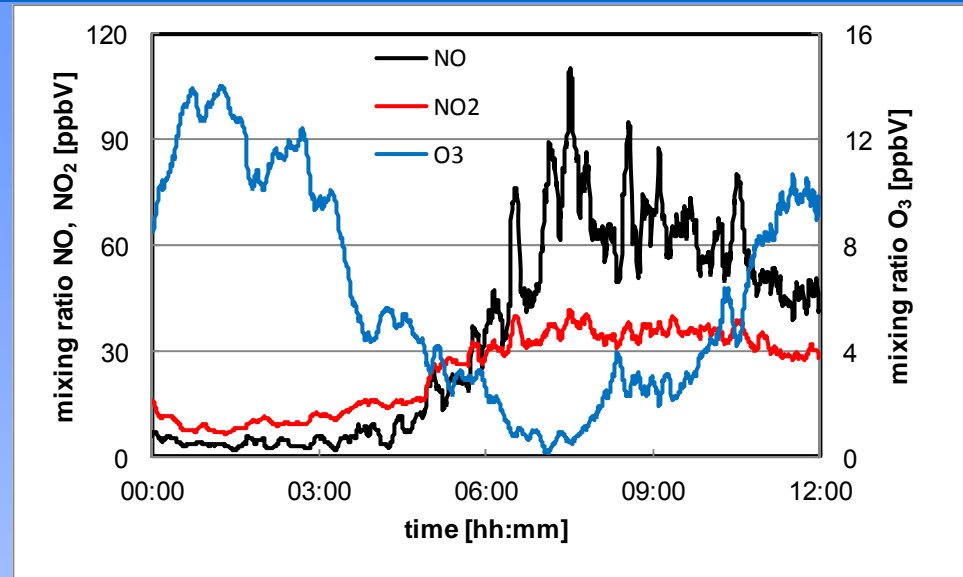
- No RO₂-chemistry; O₃-background (BG) constant:

$$\text{Ox} = (\text{NO}_2/\text{NO}_x)_{\text{direct}} * \text{NO}_x + \text{O}_3 (\text{BG}); \quad \text{Ox} = \text{NO}_2 + \text{O}_3$$

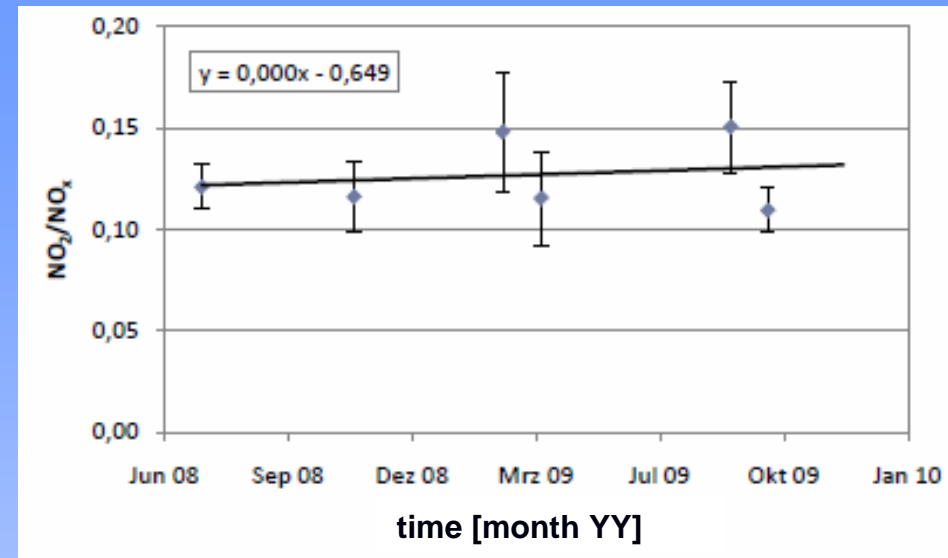
- Plot Ox versus NO_x

- Assumption: O₃ (BG) constant, high NO_x variation
- „Rush-Hour“ time (5:00 – 8:00 h)
- Strong anti-correlation between für NO and O₃
- fast secondary NO₂ formation

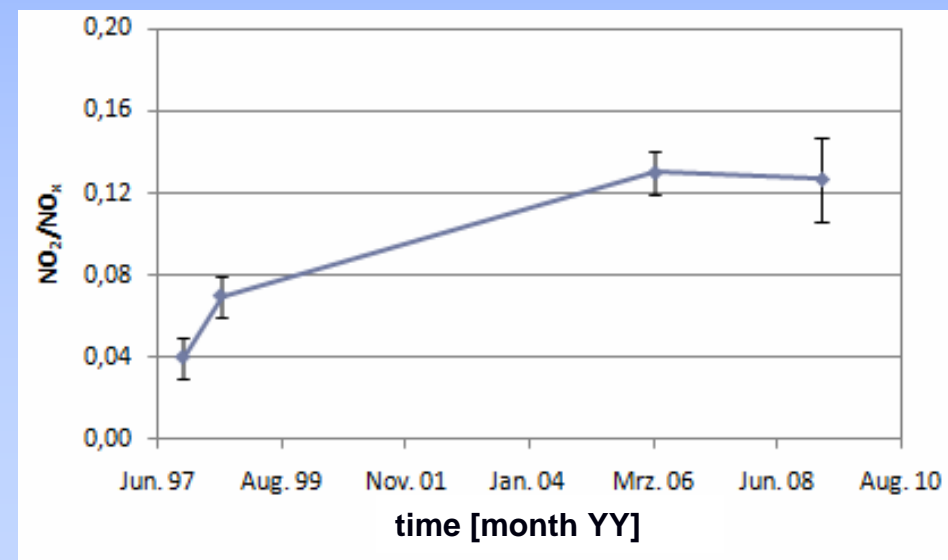
- Plot Ox vs NO_x
- $(NO_2/NO_x)_{\text{primary}} = 0.12 \pm 0.03$;
- i.e. 12 % of the NO_x are emitted as primary NO₂



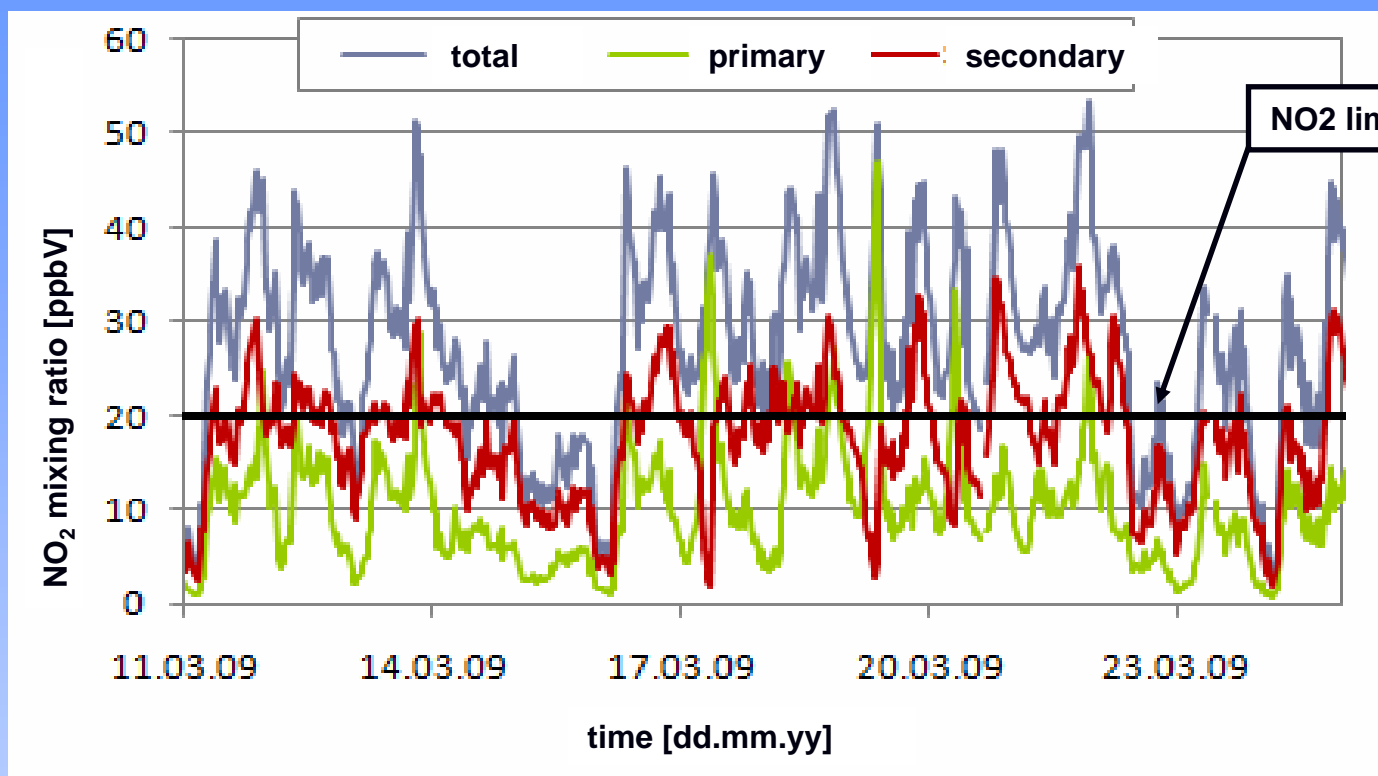
- $(\text{NO}_2/\text{NO}_x)_{\text{primary}}$ trend 2008 to 2009
- Average value: $(\text{NO}_2/\text{NO}_x)_{\text{primary}} = 0.13 \pm 0.02$



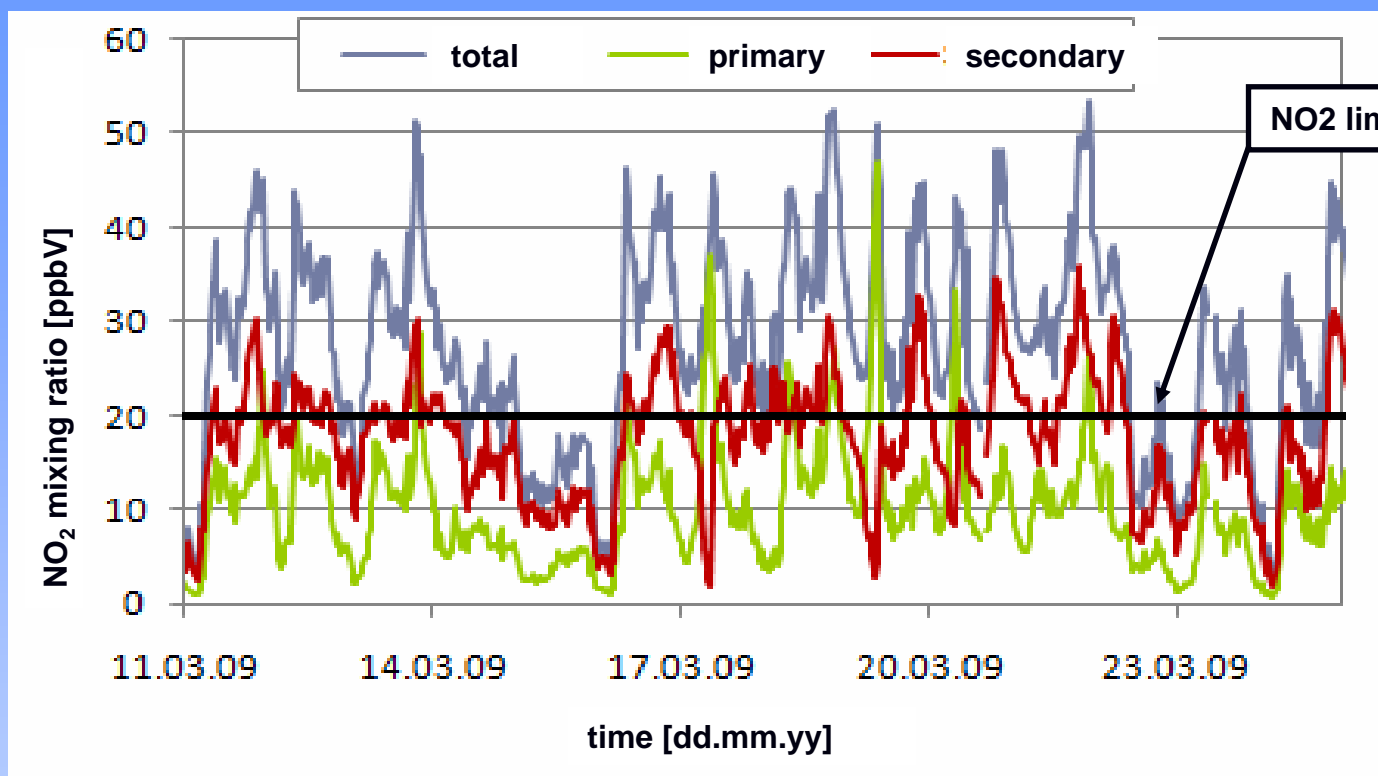
- Increasing of the NO_2 emission;
 $(\text{NO}_2/\text{NO}_x)_{\text{primary}}$ ratio
- E.g. higher emissions by modern Diesel cars...



- Emission: One reason for the stagnating NO_2
- Only reduction of $(\text{NO}_2/\text{NO}_x)_{\text{primary}}$ enough to achieve the NO_2 limit value?
- Calculation of the primary and secondary NO_2 fraction by means of the $(\text{NO}_2/\text{NO}_x)_{\text{primary}}$ ratio
- Primary $\text{NO}_2 = \text{NO}_x \cdot (\text{NO}_2/\text{NO}_x)_{\text{primary}}$ ratio
- Secondary $\text{NO}_2 = \text{rest}$



- High secondary fraction (mean 68 ± 6 %) and low primary fraction (mean 32 ± 6 %) in Wuppertal
- Hagen, Graf-von-Galen-Ring (73 ± 12 % secondary; 27 ± 12 % primary)



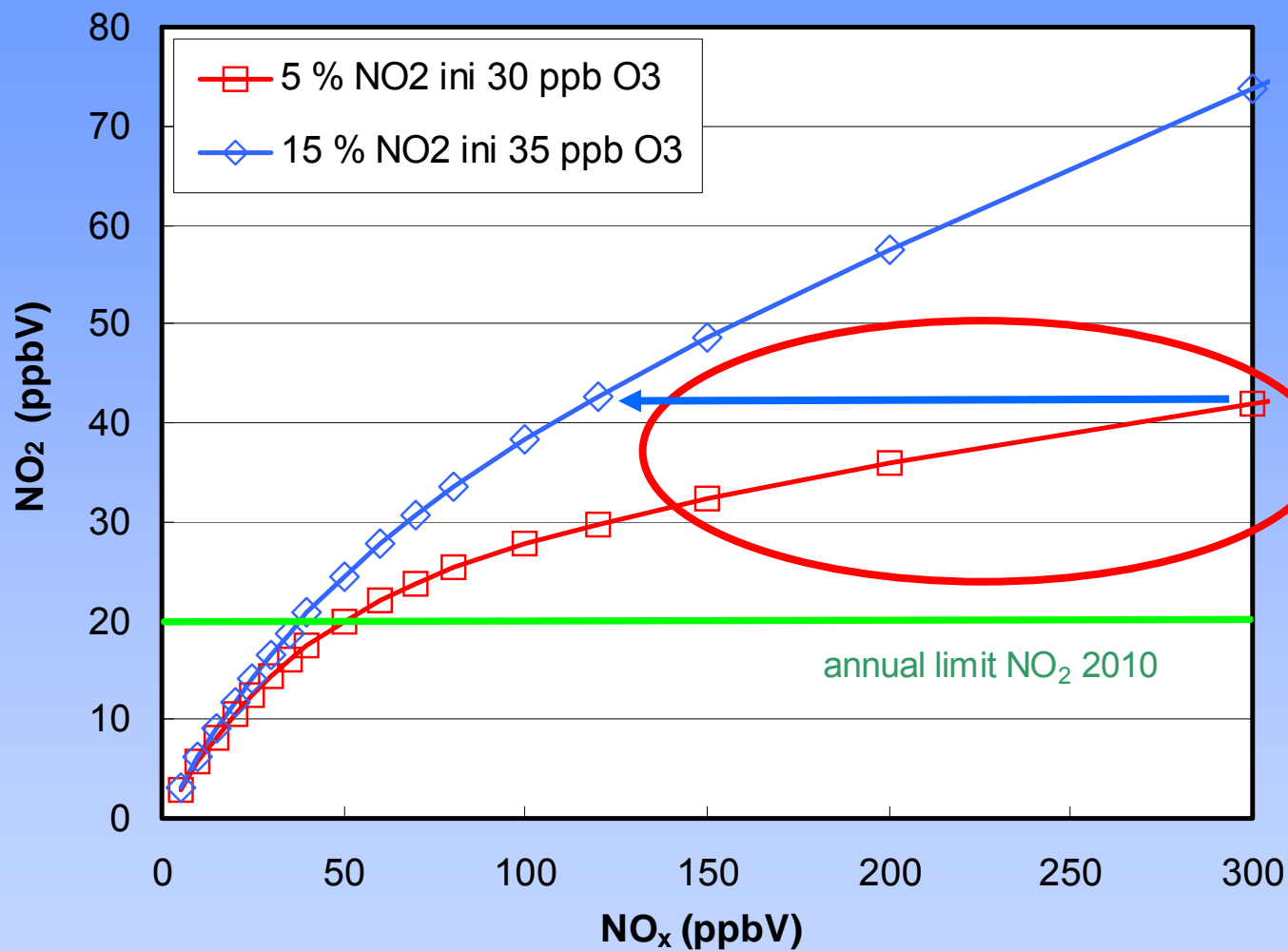
- Reduction of primary fraction to 0% not enough to achieve the NO₂ limit value (e.g. Wuppertal)
- Secondary fraction important for a efficient NO₂ reduction (e.g. Wuppertal)

○ Explanation for the observed NO_2 trend ($\text{NO}_2 \rightarrow \text{NO}_x \downarrow$)?

○ Leighton-chemistry



○ + direct emissions



Model: Leighton-chemistry, $J(\text{NO}_2) = 0.008 \text{ s}^{-1}$, (noon)

○ Explanation for the observed NO_2 trend ($\text{NO}_2 \rightarrow \text{NO}_x \downarrow$)?

○ Leighton-Chemie



○ + direct emissions

➔ Urban NO_2 problem...

○ Secondary chemistry more important!

- NO₂ not easy to measure
- NO₂(urban) still higher than the limit
- Primary NO₂ less important (~30 %) than secondary NO₂ (~70 %)
- ➔ NO_x must be further significantly reduced!
- ➔ Other instruments: photocatalysis?
- ➔ See presentation T. Flassac, my poster...



Thanks for your attention