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Primary NO₂ emissions and their impact on air quality in traffic environments in Germany

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Abstract

Background: The decreasing NO_x concentrations at urban measurement stations in Germany are in agreement with the reduction of NO_x emissions from vehicular traffic. However, the measured NO₂ concentrations are stagnating nationwide. In 2010, at more than the half of the urban measurement stations in Germany, annual mean values for NO₂ exceeded the new Europe-wide limit value of 40 µg/m³ (20 ppbv) NO₂. Similar findings are reported from many other member states of the European Union.

Results: The observed trend of the airborne NO₂ concentrations has different reasons. Firstly, the NO₂/NO_x emission ratio has increased significantly during the last two decades. Furthermore, secondary NO₂, caused by the titration reactions of NO with ozone (O₃) and peroxy radicals (RO₂), is responsible for the major fraction (approximately 70%) of the measured NO₂. However, secondary NO₂ shows a highly nonlinear dependency on NO_x and thus, is decreasing much more slowly than expected from the decreasing NO_x levels. Based on the results from the present study, the increased NO₂/NO_x emission ratio can only explain a minor fraction of the observed high airborne NO₂ concentration in the city center.

Conclusions: A further reduction of primary NO₂ emissions, due to improved exhaust gas treatment, will not have a strong influence on urban NO₂ levels, and a further significant reduction of the NO_x emissions, in particular from vehicular traffic, is necessary in order to meet the annual mean limit value for NO₂ of about 20 ppb in the future.

Keywords: Nitrogen dioxide, Air quality, Traffic emissions

Background

Fine particulate matter and nitrogen dioxide (NO₂) are the key problems for increasing air quality in Europe. Whereas particulate matter and the exceedance of PM limiting values have attracted considerable public attention during the last couple of years, the NO₂ problem is a relatively new one, which became mature through the introduction of new European limiting values in January 2010.

The reduction of nitrogen oxide (NO_x = NO + NO₂) emissions has been historically one of the key objectives for improving air quality in Europe. NO_x emissions have started to decrease considerably since the mid eighties of the last century in many European areas.

In Germany, nitrogen oxide emissions are still largely caused by road traffic. Nationwide, the share of road transport in the total NO_x emissions is currently around

60% [1]. Since the mid-80s, a significant decrease in NO_x emissions from road transport has been reported from Germany. According to emission calculations of the German Federal Environmental Agency, the decrease in total NO_x emissions between 1990 and 2005 is approximately 60% [1]. Figure 1 shows an example of NO and NO₂ concentrations measured on major roads in the German Federal State of North Rhine-Westphalia (NRW) for the period 1990 to 2008 [2].

One can see a significant decline in the annual averages of NO_x pollution from about 80 to about 40 ppbv. This decrease is in agreement with the calculated NO_x emission trends. In contrast, the NO₂ concentrations in NRW stagnate in the same period at about 23 ppbv. This trend has been also observed nationwide [3] and in other European countries [4-7].

Nitrogen dioxide is already a problem for many cities due to its toxicity and key role in the formation of tropospheric ozone [8]. In Germany in 2010, still more than half of the major roads were well above the current

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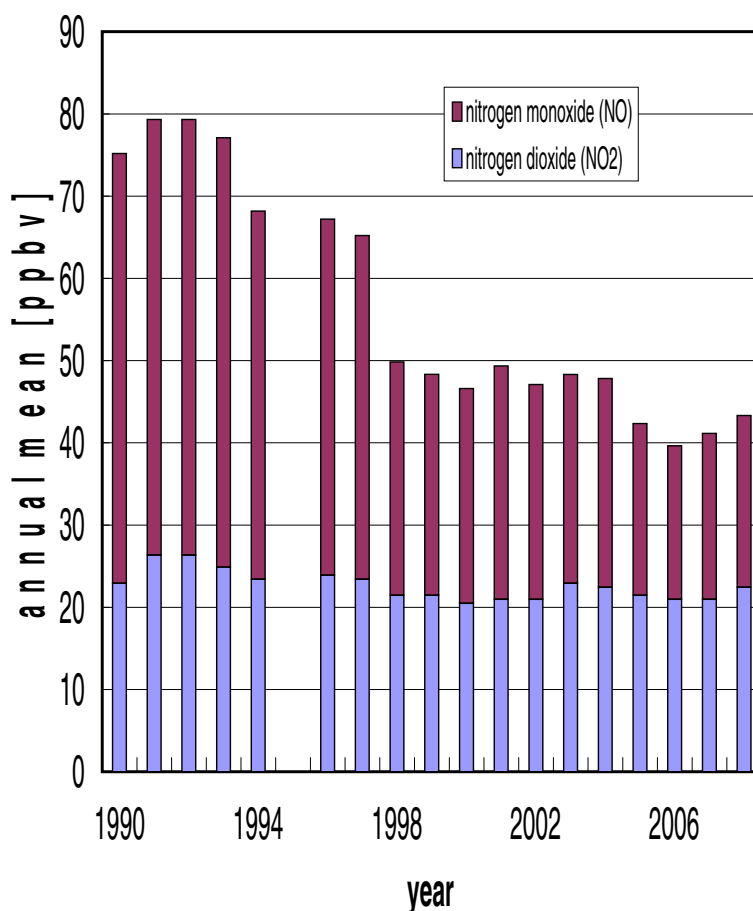


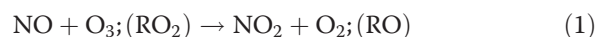
Figure 1 The NO and NO₂ concentrations. NO and NO₂ concentrations measured on major roads in the German Federal State of North Rhine-Westphalia for the period 1990 to 2008.

annual limit of 40 $\mu\text{g}/\text{m}^3$ and approximately 20 ppbv, respectively [3]. Because of the problems of many EU member states in complying with the new NO₂ annual concentration limit, the European Commission introduced time extensions to meet limits until 1 January 2015. Since early 2004, the Physical Chemistry Laboratory of the Faculty for Mathematics and Natural Sciences of the University of Wuppertal, in cooperation with the State Office for Nature, Environment and Consumer Protection (LANUV) of the German federal state of North Rhine-Westphalia performed extended pollution measurements at two monitoring stations in Wuppertal and Hagen in order to clarify the reason for the almost stagnant NO₂ pollution.

Results and discussion

Generally, in combustion processes, such as in engines of motor vehicles, NO₂ and NO are primarily formed and emitted directly. The directly emitted NO, NO (direct), is converted in the atmosphere, partly by O₃ or peroxy (RO₂) radicals into NO₂, which is called in the

following NO₂ (indirect):



In the presence of sunlight, NO₂ is partially photolysed back to NO:



Assuming that the RO₂ photochemistry is negligible at the polluted urban kerbside stations investigated and that the background O₃ concentration is constant, the level of oxidants (OX) is given by [9]:



The reason for the observed reverse trend of the NO_x and NO₂ concentrations is twofold and is an example for the complexity of the atmosphere. Firstly, the NO₂/NO_x emission ratio of road traffic has increased during the last two decades. In addition, the secondary NO₂ formed by reaction (1) has not decreased significantly

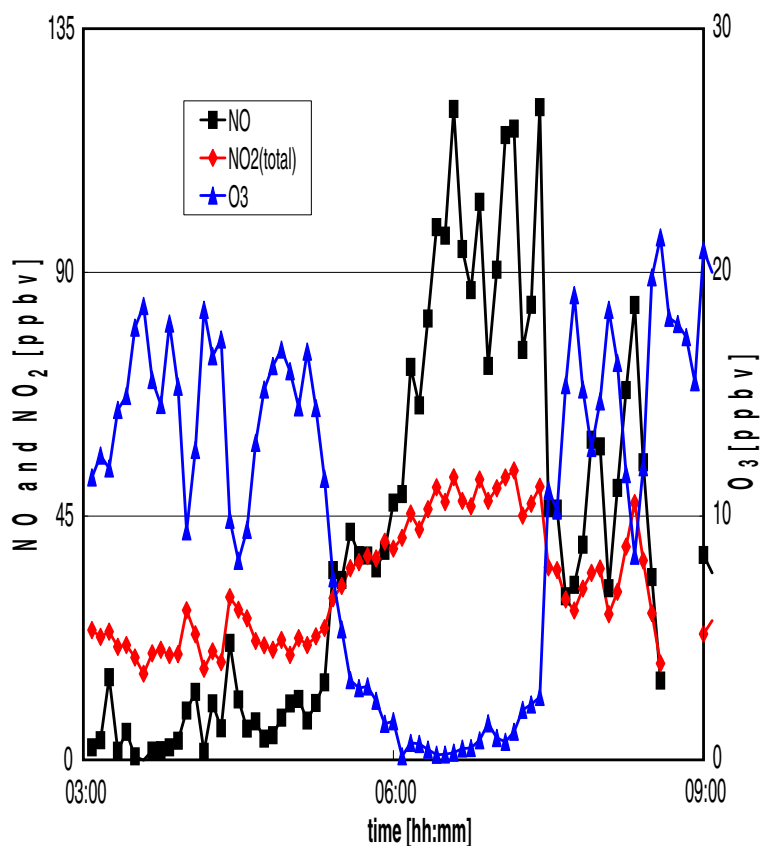


Figure 2 The NO, NO₂, and O₃ mixing ratios. NO, NO₂ and O₃ mixing ratios (5 min averaged values) at the LANUV monitoring station Wuppertal, Friedrich-Engels-Allee on 05 April 2006.

caused by the nonlinear dependency of the Leighton equilibrium, reactions (1) and (2), on the NO_x level.

To determine the NO₂/NO_x emission ratio, OX is plotted as a function of NO_x. After linear regression, one can obtain from the slope of the straight line the NO₂/NO_x emission ratio and from the intercept the O₃ background concentration [9]. The primarily emitted NO₂ is obtained by multiplying the NO₂/NO_x emission ratio with the measured NO_x concentration. The difference between the measured NO₂ (total) and the resulting primarily emitted NO₂ is then equivalent to the NO₂ (indirect), which is formed through the titration reaction of NO with ozone.

In measurements of NO, NO₂, and O₃ at busy roads in the morning during the so-called 'rush hour', usually the O₃ background concentration is almost constant, the RO₂ chemistry in the atmosphere is negligible, and the variation in the measured NO_x is largest. Accordingly, measurement data from this time interval provide the best linear correlation expected between OX and NO_x.

Figure 2 shows as an example of the NO, NO₂, and O₃ pollution of the 1 min mean values measured at the

LANUV station in Wuppertal Friedrich-Engels-Allee on 5 April 2006. One can easily determine the typical 'rush hour peak' for NO and NO₂ between 5:00 and 8:00 h in the morning. The pronounced anti-correlation between NO and O₃ is caused by the rapid formation of secondary NO₂ (indirect) through the titration reaction of NO by ozone. For the following interpretation of the OX and NO_x correlation, only the data measured between 5:00 and 8:00 h have been used.

Figure 3 exhibits the correlation between OX and NO_x in the period 5:00 to 8:00 h at the LANUV site in Wuppertal on 5 April 2006 as an example. From the linear regression a NO₂/NO_x emission ratio of (0.13 ± 0.01) and a background ozone volume mixing ratio of (32 ± 1) ppbv was obtained.

For 2006, at the monitoring station in Wuppertal, an annual average NO₂/NO_x emission ratio of (0.12 ± 0.01) and a background ozone mixing ratio of (33 ± 1) ppbv has been obtained. These values are comparable with the annual mean of (0.11 ± 0.01) for the NO₂/NO_x emission ratio and (31 ± 1) ppbv for the ozone background at the site in Hagen. For the period 2004 to 2009, at the monitoring station in Wuppertal, an average NO₂/NO_x

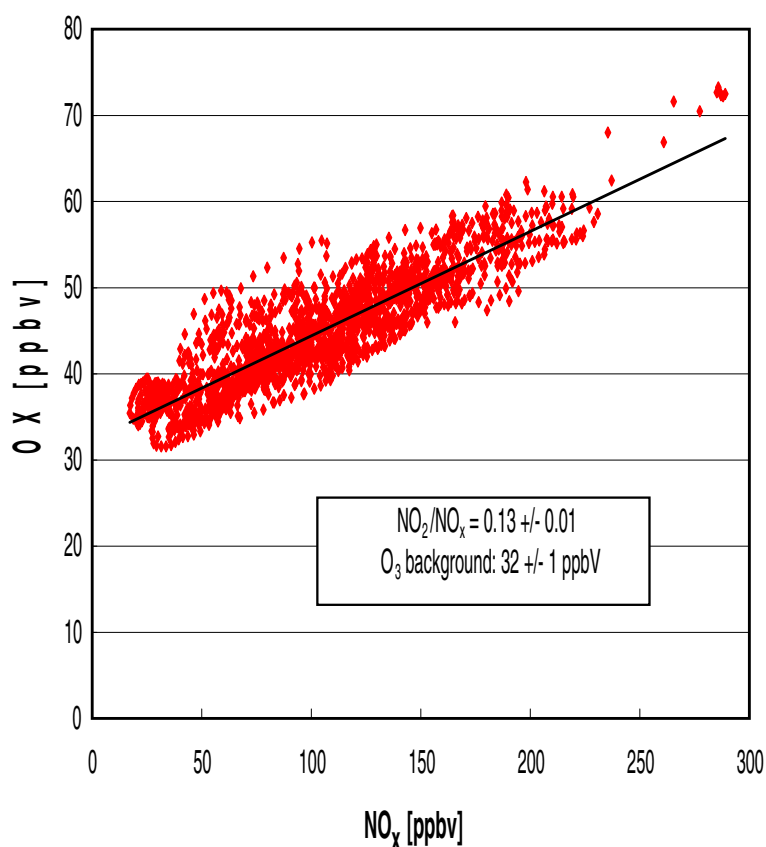


Figure 3 Plot of NO_x vs. O₃ (1 min averaged values) for the time 5:00 to 8:00 h at the LANUV monitoring station Wuppertal, Friedrich-Engels-Allee on April 05, 2006 as an example.

emission ratio of (0.13 ± 0.02) and a background ozone mixing ratio of (35 ± 2) ppbv has been obtained.

For comparison, in a traffic tunnel study of the car fleet in Wuppertal in 1997 [10], a much smaller NO₂/NO_x emission ratio of (0.04 ± 0.01) has been reported. The observed increase of the NO₂/NO_x emission ratio for road traffic and the resulting higher NO₂ emission is, thus, one reason for the observed stagnation of NO₂ pollution [11-14]. The increasing NO₂/NO_x emission ratio is caused by the rising share of diesel cars to the fleet of motor vehicles and new motor vehicle emission control systems. [15,16]

Modern diesel cars are nowadays fitted with the so-called oxidation catalysts, which significantly increase the NO₂ emission through the oxidation of NO with excess oxygen in the exhaust. Furthermore, modern diesel cars are more and more equipped with the so-called continuously regenerating particulate filters (CRT) for the deposition of soot particles in combination with an oxidation catalyst upstream of the filter. The NO₂, which is formed in the oxidation catalyst, is then used in the downstream particulate filter as an oxidant to burn the trapped soot particles. These conventional filter systems

operate with a large excess of NO₂ so that they work even under adverse operating conditions properly. However, it is worth mentioning that new regulated CRT filter systems with the so-called NOxOPT technique [17] reduce the excess NO₂ by 75% and, thus also, the direct NO₂ emissions.

Figures 4 and 5 show an example of the 30 min mean values of primary and secondary NO₂ at the LANUV station at the Graf-von-Galen-Ring in Hagen in July 2006. It is apparent that the NO₂ (indirect) already exceeded most of the time the new limit value for NO₂ (EU-2010, 40 µg/m³ to approximately 20 ppbv). In contrast, the proportion of primary NO₂ is significantly smaller.

For the monitoring station in Hagen, an annual average for the year 2006 of (35 ± 17) ppbv NO₂ was obtained, which is well above the new limit value. The NO₂ fraction, which is formed through the titration of NO with ozone contributes $(73 \pm 12\%)$ or (24 ± 4) ppbv to the total measured NO₂, whereas the direct emitted NO₂ contributes $(27 \pm 12\%)$ or (11 ± 5) ppbv, respectively. These values are comparable with the mean for the period 2004 to 2009 of $(68 \pm 6\%)$ for indirect emitted NO₂ and $(32 \pm 6\%)$ for direct emitted NO₂ at the site in

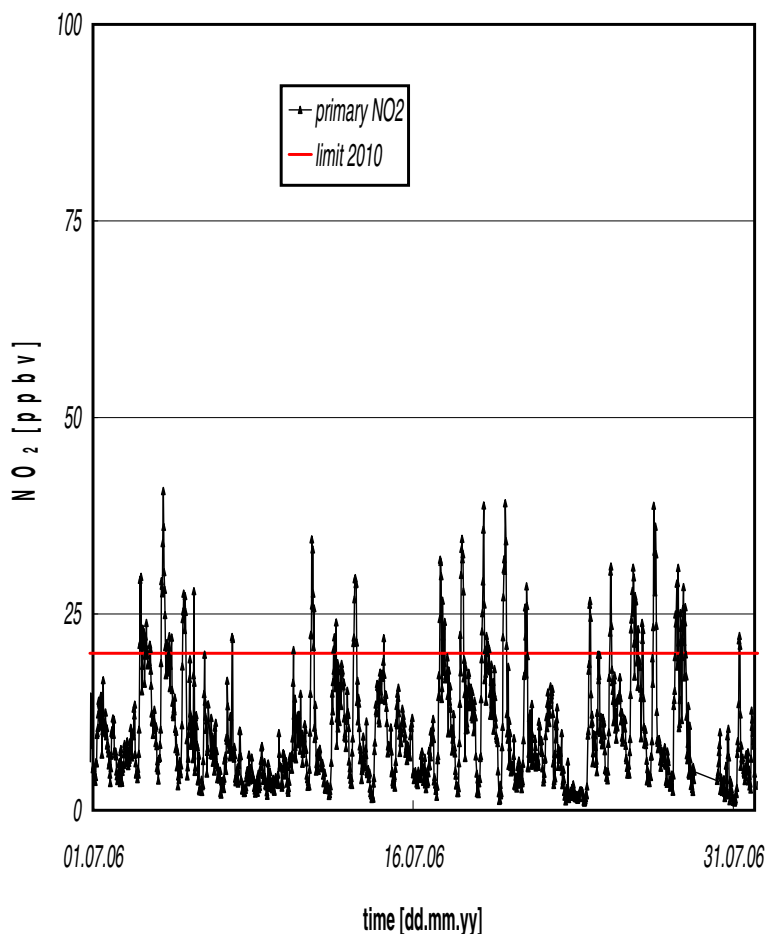


Figure 4 The plot of the primarily emitted NO_2 . Plot of NO_2 (direct) (30 min mean values), LANUV monitoring station, Graf-von-Galen-Ring, Hagen in July 2006.

Wuppertal. These results are consistent also with a study performed by the Institute for Energy and Environmental Research Heidelberg GmbH [18], which was commissioned by the Ministry of Environment of the German Federal State of Baden Wuerttemberg. Consequently, even a drastic reduction of the directly emitted NO_2 and the NO_2/NO_x emission ratio, respectively, for example through improved emission control systems [18] would not reduce NO_2 concentrations below the limiting value, since it is determined to a larger extent by secondary NO_2 formation.

In Figure 6, simple box-model calculations are shown, in which the photostationary state NO_2 mixing ratio is calculated for a background ozone level of 40 ppbv and four different NO_2/NO_x emission ratios as a function of NO_x . Only the NO_2 photolysis, reaction (2) and the ozone titration by NO , reaction (1), were considered. The rate coefficient for reaction (1) was taken from Atkinson et al. [19], and for the photolysis frequency of NO_2 , a typical noon-time summer value of $J(\text{NO}_2) = 8 \times 10^{-3} \text{ s}^{-1}$ was used.

Since secondary NO_2 is also formed in the atmosphere in the presence of hydrocarbons and sunlight through RO_2 chemistry (see above) and since $J(\text{NO}_2)$ values (NO_2 sink reaction) are often lower than used here, the actual NO_2 concentrations may be even higher.

Figure 6 shows a highly nonlinear dependence of the steady state NO_2 level with NO_x which is explained by the linear reaction kinetics of the NO_2 photolysis, sink reaction (2), and the second order kinetics of the NO_2 source reaction (1). An important conclusion from this result is that a reduction of the NO_x levels, e.g., by a factor of two will result in a much smaller reduction in the NO_2 mixing ratios, as long as the NO_x levels are significantly higher than the background O_3 levels. Thus, it is apparent that a further significant reduction of NO_x emissions is prerequisite to meet the current limit value for NO_2 , almost regardless of the NO_2/NO_x emission ratio. For example, the NO_x annual average mixing ratio in Hagen for 2007 of 92 ppbv or for Wuppertal of 55 ppbv has to be reduced to ca. 35 ppbv. This result is also consistent with other

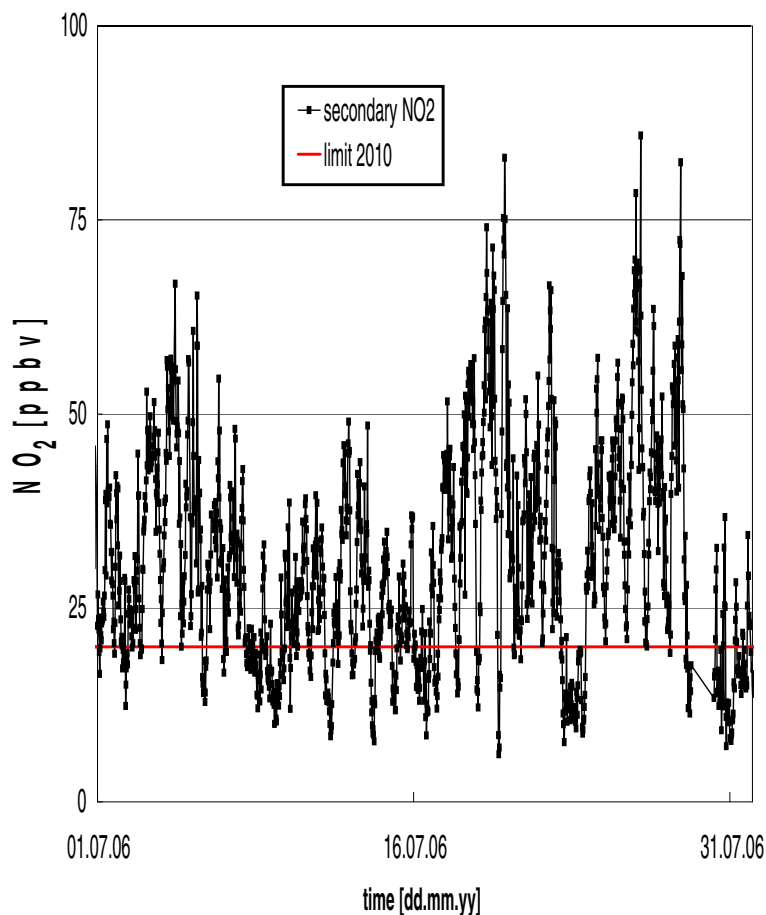


Figure 5 The plot of the secondary NO₂. Plot of the secondary NO₂ (indirect) (30 min mean values) LANUV monitoring station, Graf-von-Galen-Ring, Hagen in July 2006.

studies from Germany suggesting a further reduction of NO_x emissions of at least 50% in order to achieve the required reduction of the NO₂ concentration in the atmosphere [11,12]. A similar conclusion has been drawn also for other European Countries [5,7]. Thus, the exceedance of NO₂ limit values will remain a European problem within the next couple of years [20].

Conclusions

The observed decrease in NO_x at monitoring stations located close to road traffic is in agreement with the reduction of NO_x emissions from road transport. However, the NO₂ concentrations at these stations remained either constant or even slightly increased not only in Germany but throughout Europe. In 2010, at more than half of the monitoring stations at main roads, the NO₂ concentrations still exceeded the limit for the annual mean of 40 µg/m³ and approximately 20 ppbv, respectively.

The reason for the observed NO₂ trend is twofold. Firstly, the NO₂/NO_x emission ratio has increased significantly during the last two decades. Furthermore,

caused by the nonlinear dependency on the NO_x level, secondary NO₂ is decreasing much more slowly than expected from the decreasing NO_x levels. A detailed analysis of the data at two monitoring stations in Germany confirmed that the NO₂ concentrations are mostly determined by secondary NO₂ formation.

A reduction of the primarily emitted NO₂ (direct) due to improved emission control systems alone is not sufficient to reduce the NO₂ concentrations significantly. Compliance with the NO₂ annual limit of approximately 20 ppbv requires a further drastic reduction of NO_x emissions in the near future. However, the exceedance of NO₂ limit values will remain a European problem within the next couple of years.

Methods

Measurements of traffic-related NO, NO₂, and ozone (O₃) concentrations in the city of Wuppertal, Friedrich-Engels-Allee, and Hagen, Graf-von-Galen-Ring were carried out in the period 2004 to 2009 to determine the direct and indirect NO₂ emission of vehicular traffic.

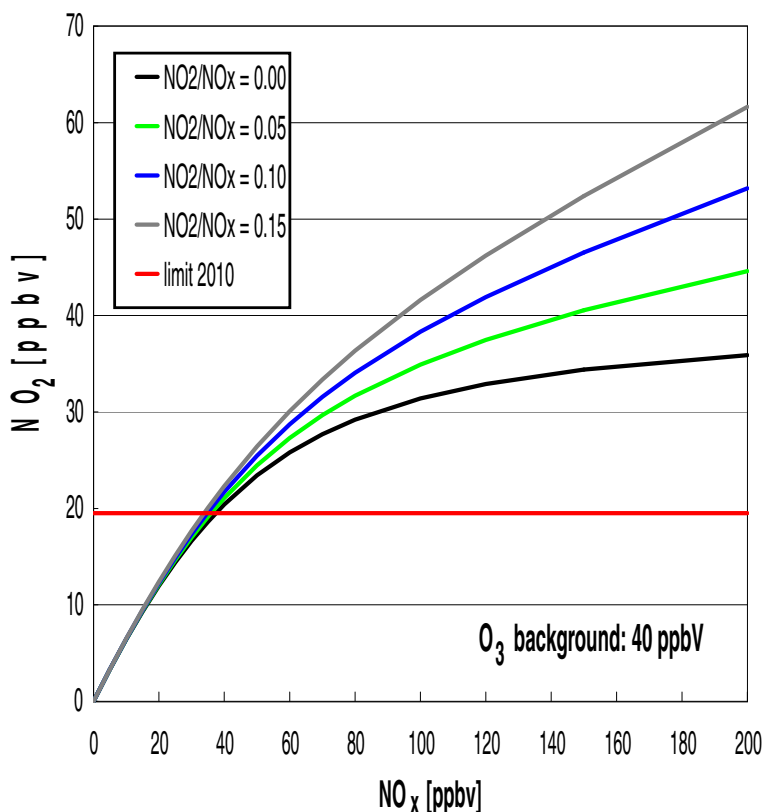


Figure 6 The photostationary mixing ratio of NO₂. Photostationary mixing ratio of NO₂ as a function of the NO_x mixing ratio, shown for different NO₂/NO_x emission ratios. Ozone background 40 ppbv, NO₂ photolysis rate $8 \times 10^{-3} \text{ [s}^{-1}\text{]}$ representing typical conditions during summertime in Germany.

Figure 7 shows the monitoring stations in Wuppertal and Hagen.

Nitrogen oxides NO and NO₂ were measured online with commercial NO_x chemiluminescence analysers (Environnemental Sat AC 31 M with molybdenum converter) and O₃ online with commercial O₃ monitors

(Environnemental Sat 41 M with UV absorption). The well-known positive interferences in the NO₂ channel of the molybdenum converter NO_x instruments by reactive nitrogen species (NO_y) was recently demonstrated to play only a minor role at kerbside stations caused by the proximity to the major NO_x source by vehicle emissions [21].



monitoring station in Wuppertal



monitoring station in Hagen

Figure 7 Monitoring stations close to main roads in Wuppertal (Friedrich-Engels-Allee) and Hagen (Graf-von-Galen-Ring).

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

PW provided the ideas and supervision and wrote the manuscript. RK and AN were primarily responsible with the support of JK for the experiments and data analyses. JK provided the box-model calculations. All contributed jointly and equally to the discussion of the manuscript. All authors read and approved the final manuscript.

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