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Non-linearity in the NO_x/NO_2 conversion

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Abstract

Non-linearity in the NO_x/NO₂ conversion

The yearly average NO₂ concentration along roads is influenced by the way it is calculated. The RIVM has analyzed the mathematical relations involved of some of the models being used in the Netherlands. With this information, the differences between model calculations as well as between models and experimental data can be understood in a better way.

On locations with a lot of traffic the yearly average limit value for NO₂ is exceeded regularly. In the Netherlands compliance with EU air quality regulations is usually checked using the results of model calculations. The models being used in the Netherlands calculate the NO₂ concentrations in several ways. It is long known that different calculation schemes produce different results. So far, the exact reasons for this were not known. By analyzing the relations that are used, the relations between calculation schemes have been determined and the differences have been quantified.

The relations between different calculation schemes have been determined for several locations of the National Air Quality measuring Network of the RIVM in the Netherlands, where yearly average concentrations are being measured. The specific location where the yearly average NO₂ is calculated, especially the type of buildings along the street and the orientation of the street, appears to have a complex influence on the relation between several calculation schemes. At present not enough field data is available to determine the relations between calculation schemes for all of the Netherlands.

Key words: Air quality, NO_x, NO₂, conversion, limit value

Rapport in het kort

Niet-lineariteit in de NO_x/NO₂ conversie

De wijze waarop de jaargemiddelde concentratie stikstofdioxide langs wegen wordt berekend, beïnvloedt de uitkomst. Het RIVM heeft de onderliggende wiskunde geanalyseerd van rekenmodellen die hiervoor in Nederland worden gebruikt. Met deze kennis kunnen de onderlinge verschillen tussen rekenmodellen onderling en tussen rekenmodellen en metingen beter worden begrepen.

Op locaties met veel verkeer wordt de gemiddelde concentratie stikstofdioxide die jaarlijks wettelijk is toegestaan vaak overschreden. In Nederland wordt deze jaargemiddelde concentratie stikstofdioxide vaak niet gemeten maar met behulp van modellen berekend. De hiervoor gebruikte modellen berekenen de jaargemiddelde concentratie stikstofdioxide op verschillende manieren. Het was al bekend dat dit tot uiteenlopende resultaten kan leiden, alleen waren de onderliggende redenen onbekend. Door de wiskundige relaties te analyseren, is aangetoond op welke manier de rekenwijzen van verschillende modellen met elkaar samenhangen en hoe de verschillende uitkomsten kunnen worden gekwantificeerd.

De relaties tussen de rekenwijzen zijn bepaald voor enkele locaties van het Landelijk Meetnet Luchtkwaliteit van het RIVM waar de jaargemiddelde concentraties worden gemeten. De locatie, vooral de bebouwing langs de straat en de ligging van de straat, blijkt invloed te hebben op de wijze waarop de rekenwijzen samenhangen. Er zijn momenteel te weinig meetgegevens beschikbaar om de wiskundige relaties tussen de verschillende rekenwijzen voor geheel Nederland in kaart te brengen.

Trefwoorden: luchtkwaliteit NO_x, NO₂, conversie, grenswaarde

Contents

Summary	6
1 Introduction	9
2 Global analysis	11
2.1 Analysis	11
2.2 Comparison to measurements	15
2.2.1 Urban situations	15
2.2.2 Rural situation	21
3 Conclusions	23
3.1 General conclusions	23
3.2 Values of the correction factors	24
References	27
Most frequently used symbols	29
Appendix 1 Detailed analysis	31
Appendix 2 NO_x/NO₂ conversion in CAR; history	49
Appendix 3 Sensitivities	53
Appendix 4 Calibration of SRM-1	57
Appendix 5 The amount of directly emitted NO₂	59

Summary

In the Netherlands several models are used to determine the NO₂ concentrations along roads. These models typically consist of a part that calculates the basic dispersion of pollutants (i.e. NO_x), while the effect on the NO₂ concentrations is then determined using an additional model. Most of the current Dutch models employ a rather simple NO_x/NO₂ conversion scheme. The relation between NO_x concentrations and NO₂ concentrations is non-linear. Due to this non-linearity, the value of the yearly averaged concentration contribution of traffic will depend on the way it is calculated. The averaged value can be obtained in three ways:

- A. from the average value of all hourly calculated concentrations contributions;
- B. from calculated yearly averaged NO_x and O₃ contributions;
- C. from calculated yearly averaged NO_x and O₃ contributions within wind sectors.

At least three effects have to be taken into account when determining the yearly averaged NO₂ concentration: (1) the non-linearity of the photo-chemical conversion function, (2) correlations between the contributions of traffic to NO emissions and O₃ background concentrations and (3) model deficiencies. The mathematical relations involved have been analyzed by the RIVM. With these, the differences between calculation schemes as well as between models and experimental data can be understood in a better way.

A correction factor has been defined to compensate for the effect of using either method B or C instead of the normal method A. A second correction factor was defined to correct for the model deficiencies. The values of the correction factors have been determined for several locations of measuring stations of the RIVM. The correction factors have been shown to depend on the distribution of NO concentrations as well as on the correlation between the NO concentrations and the O₃ background concentrations, the shape and orientation of the street as well as the exact location within a street will – to some extent – influence the values of the correction factors. These factors probably explain the relatively large variations in the values obtained for the correction factors. The consequence of such variations is that it is not currently possible to suggest using average correction factors for areas throughout the Netherlands. Furthermore, the available data are not sufficient to determine the pattern of the variations with an accuracy required to estimate their values in general situations.

The influence of the surroundings is, by definition, small in the case of a highway through an open field. However, here also the correlation between the NO and O₃ concentrations will be important. Again, not enough data is available to suggest average correction factors that can be used throughout the Netherlands.

The research presented in this report has focussed on the NO_x/NO₂ conversion model as it is presently used in several Dutch models. In principle, the same kind of analysis can be applied to other conversion schemes. Further research in this field will be conducted by the RIVM.

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1 Introduction

The most important legal limit value for nitrogen dioxide (NO₂) is the yearly averaged concentration. A legal limit value for the maximum hourly NO₂ concentration also exists, but in the Netherlands this limit value is practically never exceeded (Beijk et al., 2007). In the Netherlands several models are used to determine the NO₂ concentrations along roads. These models typically consist of a part that calculates the basic dispersion of pollutants (i.e. NO_x), while the effect on the NO₂ concentrations is then determined using an additional model. Most of the current Dutch models [Standard Calculation Model, SRM-1 for urban streets (also known as CAR) and SRM-2 for highways] employ a rather simple NO_x/NO₂ conversion scheme.

The relation between NO_x concentrations and NO₂ concentrations is non-linear. In this report the effect of this non-linear chemical relation on the yearly averaged concentration of NO₂ contributed by road traffic will be discussed. Due to this non-linearity, the value of the yearly averaged concentration contribution of traffic will depend on the calculation:

- as the average of all individual hourly values calculated for every hour;
- calculated from the yearly averaged concentration of NO or NO_x contributed by traffic, in combination with the yearly averaged ozone (O₃) concentration;
- calculated from a wind rose of yearly averaged concentrations of NO or NO_x contributed by traffic, in combination with a wind rose of yearly averaged O₃ concentration.

2 Global analysis

2.1 Analysis

The total production of NO₂ due to traffic emissions is the result of two processes – the direct emission of NO₂ by vehicles and the reaction of emitted NO with O₃, the so-called photo-conversion reaction. The average direct emission of NO₂ in 2007 amounts to 7% of the NO_x emitted by medium-duty and heavy-duty vehicles together and roughly 18% of that emitted by smaller cars. The total NO₂ concentration in the close vicinity of a road therefore consists of three parts:

total NO₂ = directly emitted NO₂ + NO₂ converted from NO + background.

The timescale of the photo-chemical reaction is in the order of several minutes. As meteorological conditions and background levels are usually assumed to be roughly constant during a 1-hour period, it would appear to be a reasonable assumption that a chemical steady-state condition exists during each 1-hour interval. The non-linearity in the averaging of the NO/NO₂ conversion is due to the photo-chemical reactions. Ozone is formed when various pollutants react under the influence of sunlight. NO molecules from the exhaust of cars and trucks react with this ozone to form NO₂. This process is called photo-conversion, and it can be described in a model using a mathematical function. We will denote the photo-conversion function by $g(n_i, o_i)$ (in µg/m³), where n_i stands for the amount of NO (µg/m³) that is available during the 1-hour measuring interval, and o_i represents the background concentration of O₃ during that hour (also in µg/m³). The following general assumptions can be made for the photo-conversion function:

- the function values, i.e. concentration of converted NO₂ are positive:

$$g(n_i, o_i) \geq 0 \quad \forall n_i, o_i \tag{1}$$

- the slope of the function is positive, with more NO leading to more converted NO₂:

$$\frac{\partial g(n_i, o_i)}{\partial n_i} > 0 \quad \forall n_i, o_i \tag{2}$$

- with increasing NO concentrations the relative amount of converted NO₂ decreases due to O₃ limitation:

$$\frac{\partial^2 g(n_i, o_i)}{\partial n_i^2} < 0 \quad \forall n_i, o_i. \tag{3}$$

The relation between the available amounts of NO and converted NO₂ is roughly as shown in Figure 1, below.

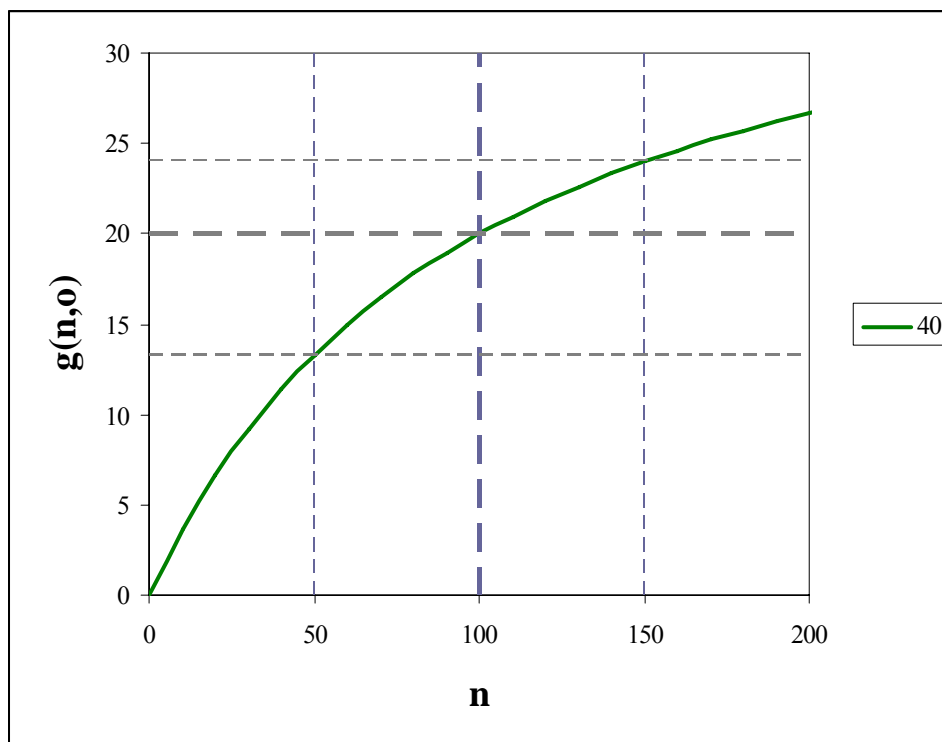


Figure 1 Typical relation between the amount of NO and converted NO₂.

The Dutch standard calculation model 2 (SRM-2), which is used along highways and large provincial roads, employs a very simple empirical relation, originally proposed by Van den Hout (1988), for the photo-chemical conversion:

$$g(n_i, o_i) = \frac{o_i \cdot n_i}{n_i + K} \quad (4)$$

where the index *i* denotes a specific hour, and the function $g(n_i, o_i)$ represents the amount of NO₂ that is converted, given a certain NO traffic contribution (n_i) and a specific O₃ background (o_i). The empirical constant K is assumed to have a value of 100 and, by definition, the same unit as the concentrations. The value of K was obtained from a comparison of measured and calculated NO₂ concentrations. The amount of NO, denoted by n_i , is a fraction of the amount of NO_x (\equiv NO + NO₂), with $n_i = (1-f) \text{NO}_{x(\text{hour}=i)}$, with f denoting the fraction of NO₂ emitted directly by the vehicles. In this report, the term ‘concentrations’ indicates ‘concentration *contributions* from traffic’. All concentrations are given in micrograms per cubic meter and NO_x concentrations are in units of NO₂. The term

‘conversion concentration’ indicates the amount of NO₂ that was converted from NO into NO₂ in a photo-chemical reaction with O₃.

As an example of the non-linear nature of averaging, let us assume a constant O₃ background concentration of 40 µg/m³. Given NO_x concentrations of 10, 100 and 190 µg/m³ during three 1-hour periods, respectively, the average value is 100 µg/m³. For these same 3 hours the function $g(n_i, o_i)$ has values of 3.6, 20.0 and 26.2 µg/m³ respectively, with an average of 16.6 µg/m³. If $g(n_i, o_i)$ is evaluated using the average NO_x and O₃ concentrations of 100 and 40 µg/m³ the result is 20 µg/m³. Clearly, the result of averaging the three hourly NO₂ concentrations (16.6) is not equal to the NO₂ concentration obtained from the average NO_x and ozone concentrations; as demonstrated, they differ by a factor of 16.6/20.0 = 0.83. In practice there are much more hours with lower NO_x contributions than there are hours with (very) high NO_x contributions and the non-linearity can be substantially larger. For a more general analysis of the above, we will initially assume (a) that relation (4) provides a good description of the hourly NO_x /NO₂ conversion process and (b) that there is a constant amount of O₃ during the entire year.

We will denote the yearly averaged value of the function $g(\)$ by¹:

$$\overline{g(n_i, o_i)}. \tag{5}$$

The average value of all hourly values n_i is denoted by \bar{n} . The function value of \bar{n} is given by

$$g(\bar{n}, o). \tag{6}$$

Given the shape of the function $g(n_i, o)$, with the assumptions (1)–(3), it is clear that for all concentration contributions $\Delta > 0$:

$$g(\bar{n} + \Delta, o) - g(\bar{n}, o) < g(\bar{n}, o) - g(\bar{n} - \Delta, o). \tag{7}$$

In case there are at least as many hours with $n_i < \bar{n}$ as there are hours with $\bar{n} < n_i$ we can deduce:

$$g(\bar{n}, o) > \overline{g(n, o)}. \tag{8}$$

Generalizing (8) to also include the effect of variations in O₃, we can write:

¹ A bar indicates time-averaging, usually over 1 year. When different averaging periods are used, these will be clearly recognizable from the context.

$$\overline{g(n, o)} = g(\overline{n}, \overline{o}) \cdot \overline{\chi} \quad (9)$$

A more detailed analysis is presented in Appendix 1. The factor $\overline{\chi}$ is shown to compensate for the average effect of both the non-linearity of the model and the effect of correlations between the NO_x contributions of the traffic and the O₃ background concentrations. This value depends on the distribution of the values for n_i and o_i . Once the distributions for the NO_x and O₃ concentrations are obtained, the value of $\overline{\chi}$ can be calculated (see Appendix 1). The RIVM has a measuring station (LML639, see Beijck et al., 2007) in the 'Erzeijstraat', a typical street canyon, that is located in the city of Utrecht. Using the measured distributions of NO contributions and O₃ background concentrations measured there in the year 2003 the value of $\overline{\chi}$ can be calculated to be 0.66. The measuring station LML640, Universiteitsbibliotheek, was used as a background station.

Thus far we have assumed that (hourly) model results are in good agreement with actual field measurements. In the case of a flawed model, however, (systematic) differences between calculated and measured concentrations may occur. When comparing calculated NO₂ conversion contributions to measured values we therefore need to introduce an additional correction factor:

$$\overline{g(n, o)}_{measured} = g(\overline{n}, \overline{o}) \cdot \overline{\theta} \quad (10)$$

The parameter $\overline{\theta}$ is the result of several effects, the non-linearity of the model as well as possible model deficiencies. From (9) and (10) we also define a correction factor for model deficiencies $\overline{\alpha}$. Whereas the value of $\overline{\chi}$ can be calculated and the value of $\overline{\theta}$ can be determined from a comparison between calculated and measured concentrations, the value of $\overline{\alpha}$ can not be determined directly. It is defined as follows:

$$\overline{\alpha} = \frac{\overline{\theta}}{\overline{\chi}} \quad (11)$$

The values of $\overline{\alpha}$ and $\overline{\theta}$ depend on many factors and are hard to estimate. For example, the NO_x background concentration does not influence the result of the conversion function (4), whereas calculations with the chemistry package of OSPM, a practical street pollution model, do indicate an influence. As a result of these mechanisms the values of $\overline{\theta}$ and $\overline{\alpha}$ may vary both in time and location and, as a result, compared to $\overline{\chi}$ they are much harder to calculate (see Appendix 1). The Dutch CAR model contains an empirically derived value of $\overline{\theta} = 0.6$ that has been derived from geometrical considerations and a comparison to a limited amount of experimental data (Eerens et al., 1993; see Appendix 2). Given the measured NO contributions of the traffic and measured O₃ backgrounds for the Erzeijstraat in 2003, we can calculate the correction factor $\overline{\theta}$ in a semi-analytical way, deriving a value of 0.71, with $\overline{\chi} = 0.66$; this results in a value of 1.08 for $\overline{\alpha}$. Using a different procedure, which

is outlined in Appendix 1, the values of $\bar{\alpha}$ and $\bar{\theta}$ can also be derived directly from hourly measurements and calculations. We then obtain $\bar{\chi} = 0.66$, $\bar{\theta} = 0.70$ and $\bar{\alpha} = 1.06$. Although calculated in a different way, the values are in good agreement.

In a number of situations, dispersion models are used to calculate the concentration contributions for a number (usually 12) of wind directions and/or wind sectors. The yearly averaged concentration is then obtained from a weighted average of the sectors. The correction factors $\bar{\alpha}_S$, $\bar{\chi}_S$ and $\bar{\theta}_S$ (the subscript S indicates averaging over wind sectors) can also be determined for the case of discrete wind sectors. The variation in O_3 concentrations within each sector is smaller than the variation over the full 360 degrees. In addition, the variation in NO_x contributions within each sector will usually be smaller and the correlation between the NO_x and O_3 will be different from that of the general case. Therefore, the results of such an analysis using wind sectors will differ from the general results that are obtained neglecting wind sectors.

2.2 Comparison to measurements

The correction factors can be determined from field measurements in cases where the NO_x and NO_2 contributions from traffic can be determined. This means that pairs of measuring stations are needed, one inside a street or next to a highway and one in a location that is representative of the background concentration. The contributions from traffic can be obtained from the concentration differences measured at these locations. Unfortunately, only a few such pairs of measuring stations are available in the Netherlands.

2.2.1 Urban situations

The values of $\bar{\chi}$, $\bar{\theta}$ and $\bar{\alpha}$ have been calculated and compared to measurements for three locations with measuring stations of the RIVM – one in a street canyon in a busy city (Utrecht: Erzeijstraat) and two near intersections of roads (Groningen: Europaweg; Nijmegen: Graafseweg). A detailed analysis for the Erzeijstraat is presented in Appendix 1. The procedure for the Europaweg and the Graafseweg is identical. In Utrecht also a measuring station is available on the Kardinaal de Jongweg. Unfortunately, the background location of Universiteitsbibliotheek does not seem to be representative for the location of the Kardinaal de Jongweg. Therefore, the data from these stations could not be combined.

In Figure 2 the wind rose of NO_x concentration contributions measured at the measuring station in the Erzeijstraat, weighted with the chance of occurring, is shown for 2003. The meteorological data are taken from Schiphol.



Figure 2 Wind rose of NO_x concentration contributions in the Erzeijstraat. LML640 was used as the background location.

For the general case of yearly averaged concentrations, the values for $\bar{\chi}$, $\bar{\theta}$ and $\bar{\alpha}$ have been determined from the available data for 1996–2003 using MATLAB, version 7. The results are plotted in Figure 3.

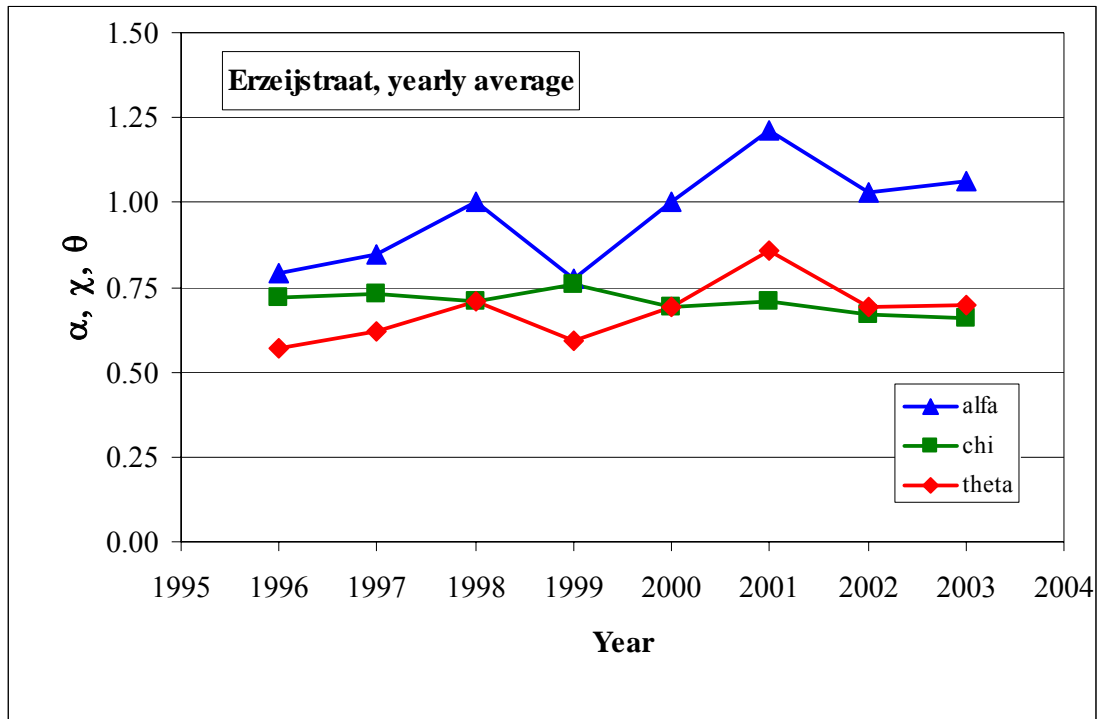


Figure 3 Values for $\bar{\chi}$, $\bar{\theta}$ and $\bar{\alpha}$ for the period 1996 up and including 2003 as obtained from field data of the RIVM.

The value of $\bar{\chi}$ varies only slightly from year to year, between 0.66 and 0.77. In comparison, the value of $\bar{\theta}$ varies substantially more – between 0.57 and 0.86, with an average value of 0.68. The average value for the period 2000–2003 is somewhat higher at 0.74. As already mentioned, the values for $\bar{\theta}$ must be compared to the value of 0.6 that is currently used in the SRM-1 model. The value of $\bar{\alpha}$ varies between 0.78 and 1.21.

The results presented in Figure 3 were obtained neglecting the variations between wind sectors. The values averaged for wind rose are presented in Figure 4 for the period 1996–2003.

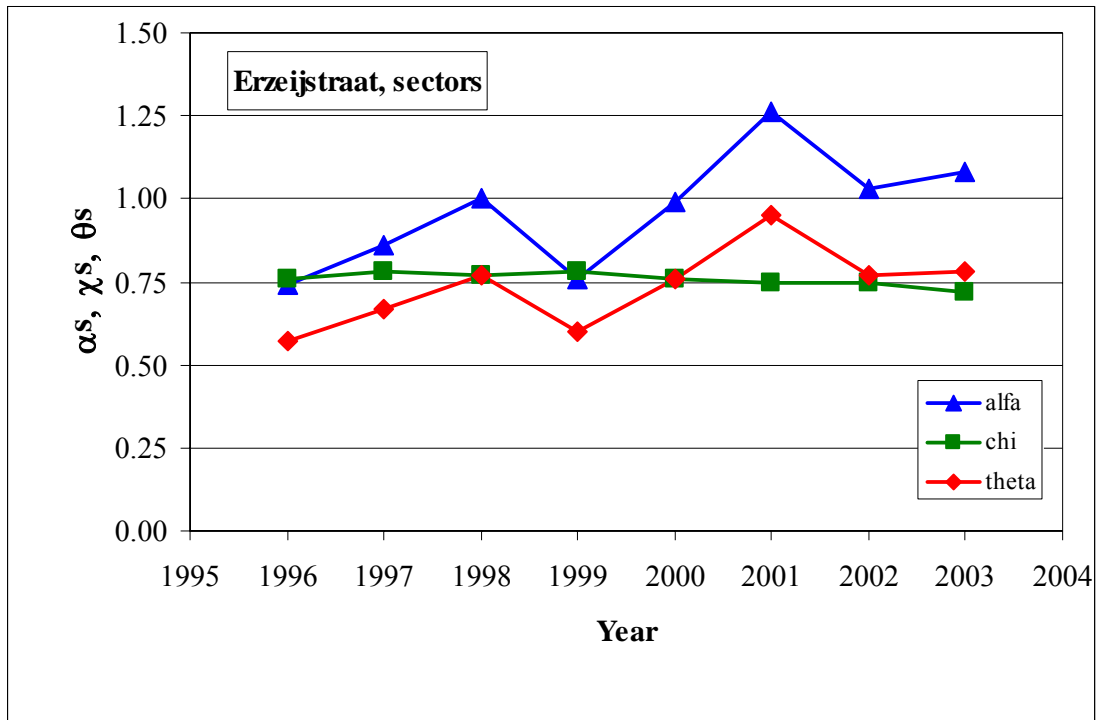


Figure 4 Values for $\overline{\theta_s}$, $\overline{\alpha_s}$ and $\overline{\chi_s}$ in the Erzeijstraat in the period 1996–2003.

Although the shapes of the curves in Figure 4 are quite similar to those in Figure 3, the values of the correction factors $\overline{\theta_s}$ are up to 8–12% higher than those obtained in the general case. In the wind rose-averaged case, the value of $\overline{\chi_s}$ varies between 0.72 and 0.78, that of $\overline{\alpha_s}$ varies between 0.57 and 0.95, with an average value of 0.73, and the average value for $\overline{\theta_s}$ over the period 2000–2003 is, as in the field data, somewhat higher at 0.82. Data are still available for the Erzeijstraat measuring station, but in 2003 the background measuring station in Utrecht ('Universiteitsbibliotheek') was rendered inoperative. As a result, it has not been possible to analyse NO₂ conversion in recent years.

More recently, new background/street station combinations have been commissioned in Groningen, Nijmegen and Breda. The street station in Breda does not provide data for NO₂ and NO_x; however, 3 and 4 years of valid data are available for Groningen and Nijmegen, respectively. The data from these latter two locations have been used to perform analyses similar to those carried out on the Erzeijstraat datasets. As there are no O₃ measurements available for the street locations in Nijmegen and Breda, it has not been possible to determine the direct NO₂ emission from the field measurements. A value based on traffic emission factors was therefore calculated, which resulted in a relatively high uncertainty in the values of $\overline{\theta_s}$ and $\overline{\alpha_s}$. The value of $\overline{\chi_s}$ can be determined with a higher accuracy as this parameter

is not very sensitive to the value of the direct NO₂ fraction (see Appendix 3). The results of the analyses are shown in Figures 5 and 6.

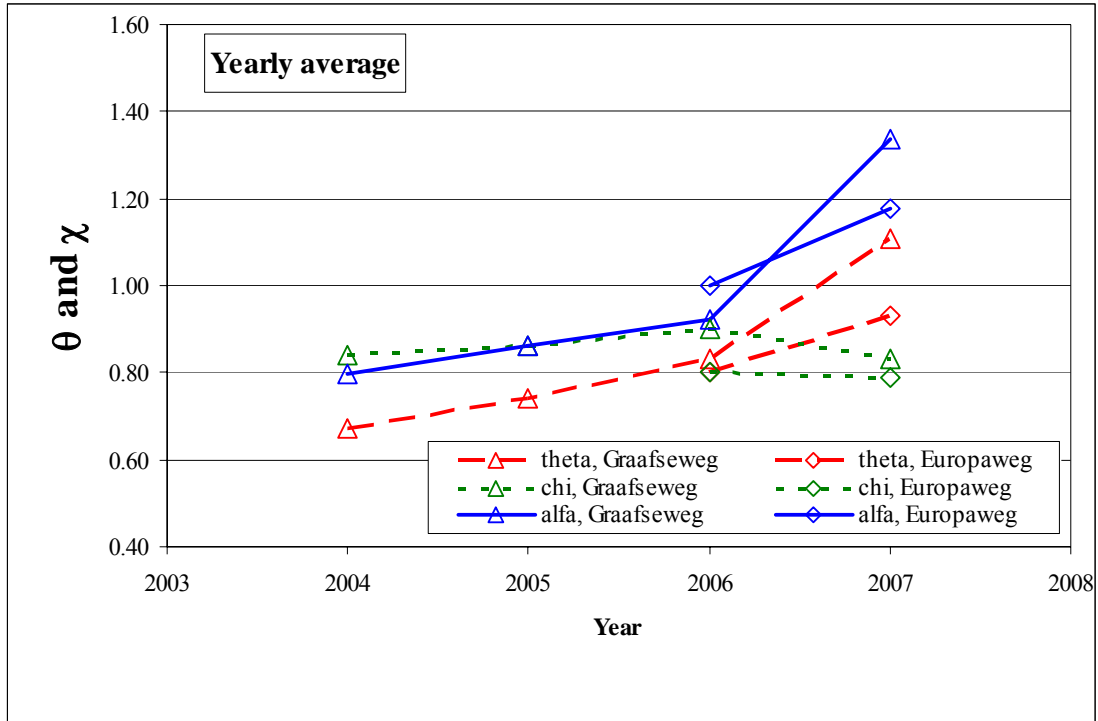


Figure 5 Values for $\bar{\theta}$, $\bar{\chi}$ and $\bar{\alpha}$ for the period 2004 up to and including 2007 for the Graafseweg (Nijmegen) and Europaweg (Groningen).

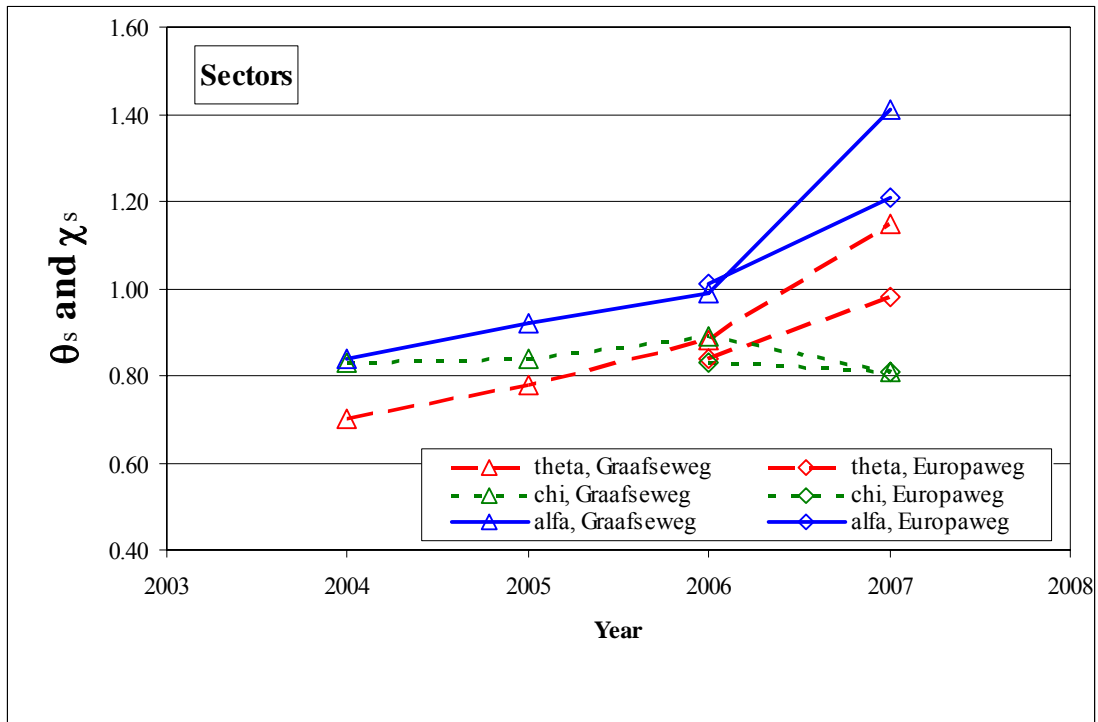


Figure 6 Values for $\bar{\theta}_s$, $\bar{\chi}_s$ and $\bar{\alpha}_s$ for the Graafseweg (Nijmegen) and Europaweg (Groningen).

The values for the correction factors $\bar{\theta}$ and $\bar{\theta}_s$ and, therefore, also for $\bar{\alpha}$ and $\bar{\alpha}_s$ increase substantially in 2007, but the reason for this is not clear. The correction factors $\bar{\chi}$ and $\bar{\chi}_s$ for the locations in Groningen and Nijmegen are also approximately 12–22% higher than those obtained for the Erzeijstraat. Given the underlying mathematical structure of χ , these differences may be due to the street canyon type of the Erzeijstraat versus the much more open character of the other locations. The result of these differences is that the distribution of NO_x contributions as well as the correlation between the NO_x and ozone will be different. The values for $\bar{\theta}$ and $\bar{\theta}_s$ and also those of $\bar{\alpha}$ and $\bar{\alpha}_s$ are roughly comparable to those obtained in the Erzeijstraat. The yearly variation in these values is quite substantial.

Wesseling and Sauter (2007) carried out a calibration study of the SRM-1 model in 2007 and observed that the calculated values of the NO_2 contribution at the Groningen and Nijmegen locations substantially underestimated the measured values. These contributions were calculated using the standard setting of SRM-1, in which the amount of converted NO_2 is scaled by a factor of 0.6. Based on the analyses reported here, it would appear that this value of 0.6 is not suitable for these locations and that values of 0.80 (Groningen) and 0.84 (Nijmegen) would be more appropriate. This supposition was

verified when these latter values were used in the calibration instead of 0.60, and a better agreement was subsequently found between calculated and measured NO₂ contributions, see Appendix 4.

2.2.2 Rural situation

Figure 7 shows the 2003 wind rose of NO_x contributions that were determined at measuring station LML641, located close to Breukelen. The meteorological data are taken from Schiphol.

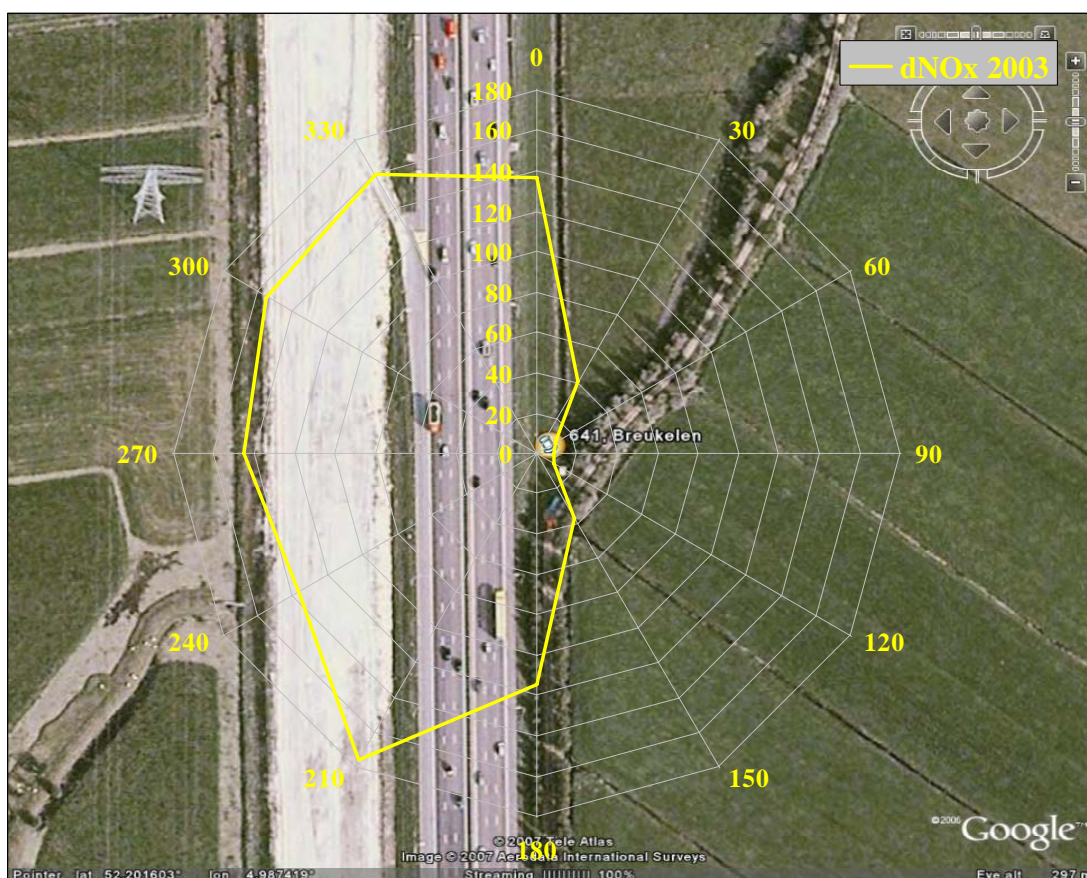


Figure 7 The wind rose of NO_x contributions at the LML641 measuring station (Breukelen) in 2003.

The measuring station is situated directly beside a busy highway, the A2, which, at that location, runs almost perfectly north–south. Some 150,000 vehicles pass the station each day, of which roughly 10% consist of medium-duty and heavy-duty traffic vehicles.

A detailed analysis of the Breukelen location is presented in Appendix 1. For the case of wind sector-averaged concentrations, the values for $\overline{\alpha}_s$, $\overline{\chi}_s$ and $\overline{\theta}_s$ (for the wind sectors influenced by the road

emissions) are determined from the available data for 1996 to 2007 using MATLAB, ver. 7. The results are plotted in Figure 8.

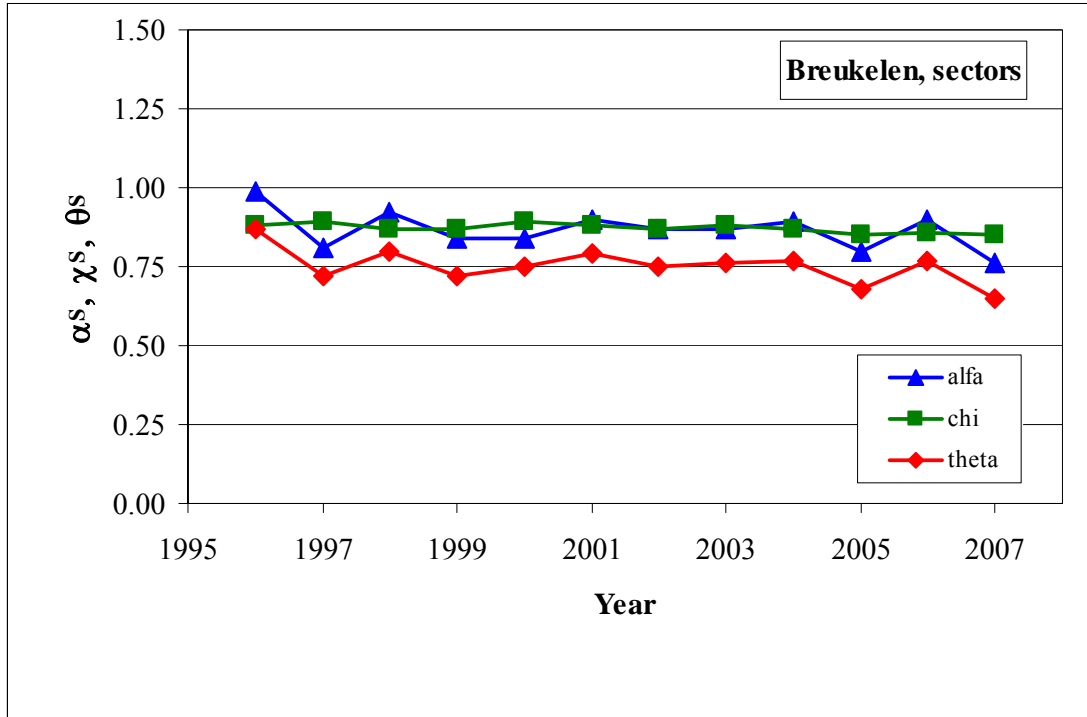


Figure 8 Values for $\overline{\alpha_s}$, $\overline{\chi_s}$ and $\overline{\theta_s}$ for the period 1996 up to and including 2007 as obtained from field data of the RIVM for the Breukelen measuring station.

The values can be seen to be quite constant over the whole period. The value of $\overline{\theta_s}$ varies slightly, with an average value of 0.75; the value of $\overline{\alpha_s}$ also varies slightly, with an average value of 0.87. The value of $\overline{\chi_s}$ is practically constant at 0.87.

3 Conclusions

3.1 General conclusions

The objective of this report was to demonstrate how the exact value of the calculated yearly averaged value of the NO₂ contribution of traffic is influenced by the approach used to determine its value. This averaged value can be obtained in three ways:

- A. from the average value of all hourly calculated concentrations contributions;
- B. from calculated yearly averaged NO_x and O₃ contributions;
- C. from calculated yearly averaged NO_x and O₃ contributions within wind sectors.

At least three effects have to be taken into account when determining the yearly averaged NO₂ concentration: (1) the non-linearity of the photo-chemical conversion function, (2) correlations between the contributions of traffic to NO emissions and O₃ background concentrations and (3) model deficiencies.

A correction factor $\bar{\chi}$ has been used to compensate for the effect of using either method B or C instead of the 'normal' method A; $\bar{\chi}$ corrects the effect of averaging the non-linear photo-chemical conversion function. A second correction factor, $\bar{\alpha}$, corrects the model deficiencies (in the case of an ideal model, $\bar{\alpha} = 1$); it is used in all three methods mentioned above. The overall correction factor is $\bar{\theta} = \bar{\alpha} \bar{\chi}$. The values of the correction factors have been determined for several locations of measuring stations of the RIVM. The value of $\bar{\chi}$ seems quite stable in time for each location. The values of $\bar{\theta}$, and therefore also of $\bar{\alpha}$, can change substantially over time.

As the correction factors have been shown to depend on the distribution of NO concentrations as well as on the correlation between the NO concentrations and the O₃ background concentrations, the shape and orientation of the street as well as the exact location within a street will – to some extent – influence the values of the correction factors. These factors probably explain the relatively large variations in the values obtained for the correction factors. The consequence of such variations is that it is not currently possible to suggest using average correction factors for areas throughout the Netherlands. An additional factor is that available data are not sufficient to determine the pattern of the variations with an accuracy required to estimate their values in general situations.

The influence of the surroundings is, by definition, small in the case of a highway through an open field. However, here also the correlation between the NO and O₃ concentrations will be important.

Again, not enough data is available to suggest average correction factors that can be used throughout the Netherlands.

The research presented in this report has focussed on the NO_x/NO₂ conversion model as it is presently used in several Dutch models. In principle, the same kind of analysis can be applied to other conversion schemes. Further research in this field will be conducted by the RIVM.

3.2 Values of the correction factors

Ad A.

For method A, it is important to determine how well the calculated concentrations are in agreement with reality (field measurements). An average correction factor, $\bar{\alpha}$, can be defined to describe how well the model calculations and measurements agree. For the location of the Erzeijstraat in Utrecht, the NO₂ conversion routine being used in the Dutch model SRM-2 requires values of $\bar{\alpha}$ between 0.78 and 1.21 for the years from 1996 up to and including 2003, with an average of 0.96. Concentrations determined using method A are unbiased and do not need any corrections for non-linearity in obtaining the yearly averaged NO₂ concentration due to traffic.

Ad B.

For method B, which is used in the Dutch SRM-1 model, model deficiencies also have to be corrected for. An additional factor that must be considered is the important effect of the non-linearity of the photo-chemical conversion. A correction factor, $\bar{\chi}$, can be derived for this effect, and in several urban situations that have been investigated it varies between 0.66 and 0.90 in the period 1996–2007. When model deficiencies of SRM-1 are also taken into account, the overall correction factor $\bar{\theta}$ varies between 0.57 and 1.11. The value for the overall correction must be compared to the value of 0.6 that is used in the Dutch SRM-1.

Ad C.

For method C, the same points should be taken into account as when using method B. The variation in O₃ concentrations is smaller within each sector than that over the full 360 degrees. In addition, within each sector the variation in NO_x contributions will usually be smaller and the correlation between the NO_x and O₃ will be different from the general case. For urban locations, the value of $\bar{\chi}_S$ (weighted average over all wind sectors S) varies between 0.72 and 0.89. The value of $\bar{\theta}_S$ varies between 0.57 and 1.15.

Using method C for a highway through an open field results in values for the correction factors that are quite constant in time. The value of $\overline{\theta}_s$ varies slightly between 0.65 and 0.87, with an average value of 0.75. Similarly, the value of $\overline{\alpha}_s$ varies slightly between 0.76 and 0.99, with an average value of 0.87. The value of $\overline{\chi}_s$ is practically constant at 0.87.

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Most frequently used symbols

$\alpha(n, o)$	correction factor to compensate for model deficiencies (no units)
$\overline{\alpha}_{(S)}$	average value of the correction factor for model deficiencies (no unit); the subscript S indicates averaging within one wind direction sector
$\overline{\beta}_{(S)}$	the average value of the correction factor for the effect of averaging the NO part of the non-linear conversion function (no unit)
$\overline{\chi}_{(S)}$	the average value of the correction factor for the effect of averaging the NO and O ₃ parts of the non-linear conversion function (no unit)
$\overline{\theta}_{(S)}$	the average value of the combined effect of the corrections factors for model deficiencies and averaging the non-linear function (no unit)
c_i^m	the measured amount of converted NO ₂ in hour i (µg/m ³)
c_i^c	de calculated amount of converted NO ₂ in hour i (µg/m ³)
\overline{c}_S^m	the average measured amount of converted NO ₂ (in wind sector S) (µg/m ³)
\overline{c}_S^c	the average calculated amount of converted NO ₂ (in wind sector S) (µg/m ³)
f	the fraction of NO ₂ directly emitted by traffic (no unit)
$g(n_j, o_j)$	the (assumed) photo-chemical conversion function (no unit)
$H(n, o)$	the number of hours within a year having an NO contribution n and an O ₃ background concentration of o (no unit)
$F(x, \mu, \sigma, \delta)$	log normal function with parameters μ, σ, δ (no unit)
K	conversion constant with empirical value of 100
n_i	the NO traffic contribution within hour i (µg/m ³)
\overline{n}	the yearly averaged NO concentration (µg/m ³)
o_i	the O ₃ traffic contribution within hour i (µg/m ³)
\overline{o}	the yearly averaged O ₃ concentration (µg/m ³)

Appendix 1 Detailed analysis

Introduction

The example in chapter 2 illustrates the difference in the result due to the order of the operations – first calculating the NO_x/NO₂ conversion versus first calculating the yearly averaged concentrations. Given a set of values {*n_i*} during a 1-year period, with an average value \bar{n} , we can define a set of hourly factors { β_i } by which $g(n_i, o)$ differs from $g(\bar{n}, o)$. This can be written as:

$$\beta_i(n_i) = \frac{g(n_i, o)}{g(\bar{n}, o)} = \frac{n_i(\bar{n} + K)}{\bar{n}(n_i + K)} \quad (\text{A1-1})$$

The average correction factor $\bar{\beta}$, given by the ratio of $\overline{g(\bar{n}, o)}$ and $\overline{g(n, o)}$, can be written as the average correction factor $\beta_i(n_i)$ for each possible value of *n_i*, weighted by the chance of occurring (*F*):

$$\bar{\beta} = \frac{\overline{g(n, o)}}{\overline{g(\bar{n}, o)}} = \sum_j F_j \beta(n_j) \quad (\text{A1-2})$$

The frequency distribution for the NO_x contributions is needed to be able to calculate the value of $\bar{\beta}$. This can be obtained from the field measurements. Figure A-1 shows the frequency of observed NO_x concentration contributions:

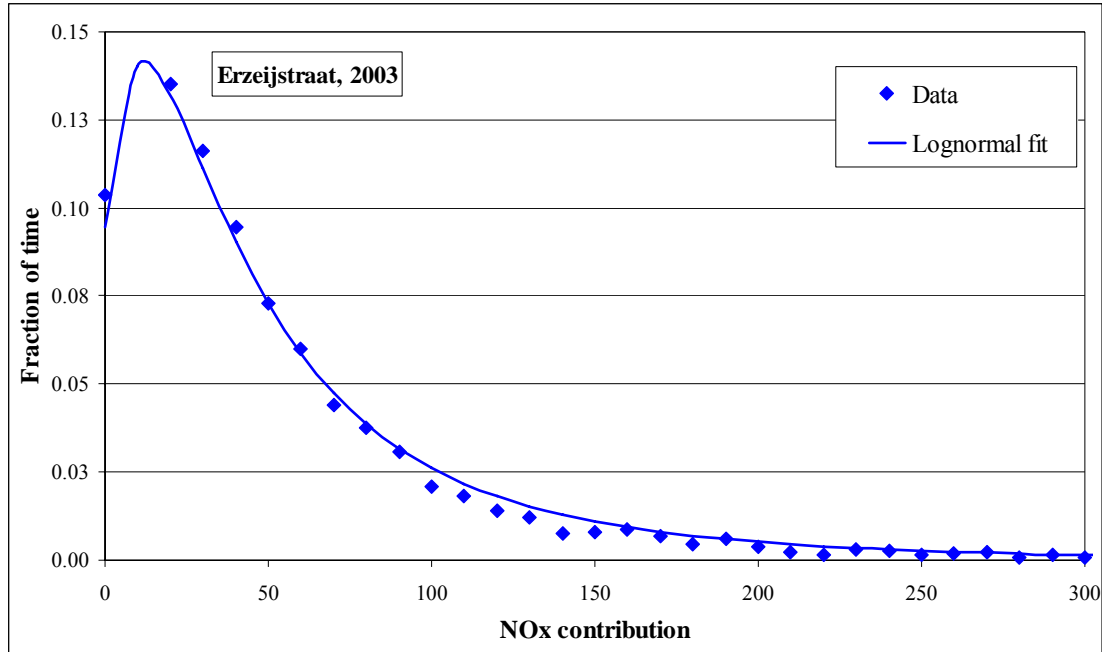


Figure A1-1 Distribution of NO_x concentration contributions as measured in the Erzeijstraat. Location LML640 was used to provide the background levels.

The frequency distribution $F()$ closely follows a three-parameter lognormal distribution given by:

$$F(x, \mu, \sigma, \delta) = \frac{e^{-\frac{1}{2}\left(\frac{\ln(x+\delta)-\mu}{\sigma}\right)^2}}{(x+\delta)\sigma\sqrt{2\pi}} \quad (\text{A1-3})$$

with x being the NO_x contributions and δ , μ and σ being the shape parameters of the distribution. The average NO_x contribution is $\bar{x} = \delta + e^{(\mu + \frac{1}{2}\sigma^2)}$. For the above data the values $\delta = 10$, $\mu = 3.86$ and $\sigma = 0.88$ yield a satisfactory description of the data². The total correction factor can now be written as:

$$\bar{\beta} = \int F(x) \beta(x) dx \quad (\text{A1-4})$$

Using relations (10) and (11), this can be written as

$$\bar{\beta} = \int_0^{N_{\max}} \frac{1}{2} \sqrt{2} \frac{x((1-f)(\delta + e^{\mu+0.5\sigma^2}) + K)e^{-0.5(\ln(x+\delta)-\mu^2)/\sigma^2}}{\sigma\sqrt{\pi}(\delta + e^{\mu+0.5\sigma^2})(x(1-f) + K)(x + \delta)} dx \quad (\text{A1-5})$$

² The shape parameters have been obtained using Maple, version 11.

with N_{max} being the maximum NO_x concentration contribution that can reasonably occur. The integral has been evaluated using the shape parameters obtained from the fit and a value of 0.66 obtained. This factor compensates for the fact that the yearly averaged NO_2 calculated from individual hours yields a result that differs from a yearly averaged NO_2 calculated from yearly averaged NO_x and O_3 concentrations.

The numerical effect of averaging the NO_x with varying O_3

The amount of converted NO_2 depends on the amount of available O_3 . The effect of the O_3 can be included in our analysis. The amount of converted NO_2 for an hourly NO concentration n_j and an hourly ozone concentration o_j is given by:

$$g(n_i, o_i) = \frac{o_i \cdot n_i}{n_i + K} \quad (\text{A1-6})$$

Using relation (9) we can write the above:

$$\text{NO}_2 \text{ (conversion part)} = \beta(n_i) \cdot g(\bar{n}, o_i) \quad (\text{A1-7})$$

The effect of the O_3 can be written as a function of the actual hourly value and the yearly averaged value (\bar{o}):

$$g(n_i, o_i) = \beta(n_i) \cdot \gamma(o_i) \cdot \frac{\bar{o} \cdot \bar{n}}{n + K} \quad (\text{A1-8})$$

with β given by (9) and γ is defined as:

$$\gamma(o_i) = \frac{o_i}{\bar{o}} \quad (\text{A1-9})$$

Although $g(n_i, o_i)$ is directly proportional to γ , non-linear effects in the averaging procedure can not be excluded due to a possible correlation between β and γ . The calculated yearly average conversion contribution can be obtained from a direct summation:

$$\overline{g(n, o)} = \frac{\bar{o} \cdot \bar{n}}{n + K} \left(\frac{1}{M} \sum_{i=\text{all hours}} \beta(n_i) \cdot \gamma(o_i) \right) = g(\bar{n}, \bar{o}) \left(\frac{1}{M} \sum_{i=\text{all hours}} \beta(n_i) \cdot \gamma(o_i) \right) \quad (\text{A1-10})$$

with M being the number of (valid) hours in a year. Equation (17) can also be written as:

$$\overline{g(n, o)} = g(\bar{n}, \bar{o}) \cdot \overline{\beta_i \cdot \gamma_i}$$

With the definitions $\delta\beta_i = \bar{\beta} - \beta_i$ and $\delta\gamma_i = \bar{\gamma} - \gamma_i$, the sum (17) can be rewritten as:

$$g(\bar{n}, \bar{o}) \cdot \frac{1}{M} \sum_i (\bar{\beta} - \delta\beta_i) \cdot (\bar{\gamma} - \delta\gamma_i) = g(\bar{n}, \bar{o}) \cdot \frac{1}{M} \sum_i (\bar{\beta} \cdot \bar{\gamma} - \delta\beta_i \cdot \bar{\gamma} - \bar{\beta} \cdot \delta\gamma_i + \delta\beta_i \cdot \delta\gamma_i)$$

From the definitions, it follows that $\overline{\delta\beta_i} = \overline{\delta\gamma_i} = 0$, $\bar{\gamma} = 1$ and that the sum can be written as:

$$g(\bar{n}, \bar{o}) \cdot \frac{1}{M} \sum_i (\bar{\beta} + \delta\beta_i \cdot \delta\gamma_i) = g(\bar{n}, \bar{o}) \cdot \left(\bar{\beta} + \frac{1}{M} \sum_i \delta\beta_i \cdot \delta\gamma_i \right) \quad (\text{A1-11})$$

We ultimately obtain:

$$\overline{g(n_i, o_i)} = g(\bar{n}, \bar{o}) \cdot \left(\bar{\beta} + \overline{\delta\beta_i \cdot \delta\gamma_i} \right) \quad (\text{A1-12})$$

Therefore, in addition to the basic non-linearity of β , the possible correlation between β and γ further complicates the relation between hourly concentrations and the yearly average. Such a correlation can occur, for example, when the street is located such that the concentration contribution from the traffic is large for those wind directions for which the O₃ background is also large. If there is no correlation, then by definition, $\overline{\delta\beta_i \cdot \delta\gamma_i} = 0$.

We describe the number of hours in a year with NO contribution n and O₃ background concentration o by a distribution $H(n, o)$. The measured distribution function $H(n, o)$ for the Erzeijstraat in 2003 is presented in Figure A1-2. Both the O₃ concentrations and NO contributions are in steps of 10 µg/m³.

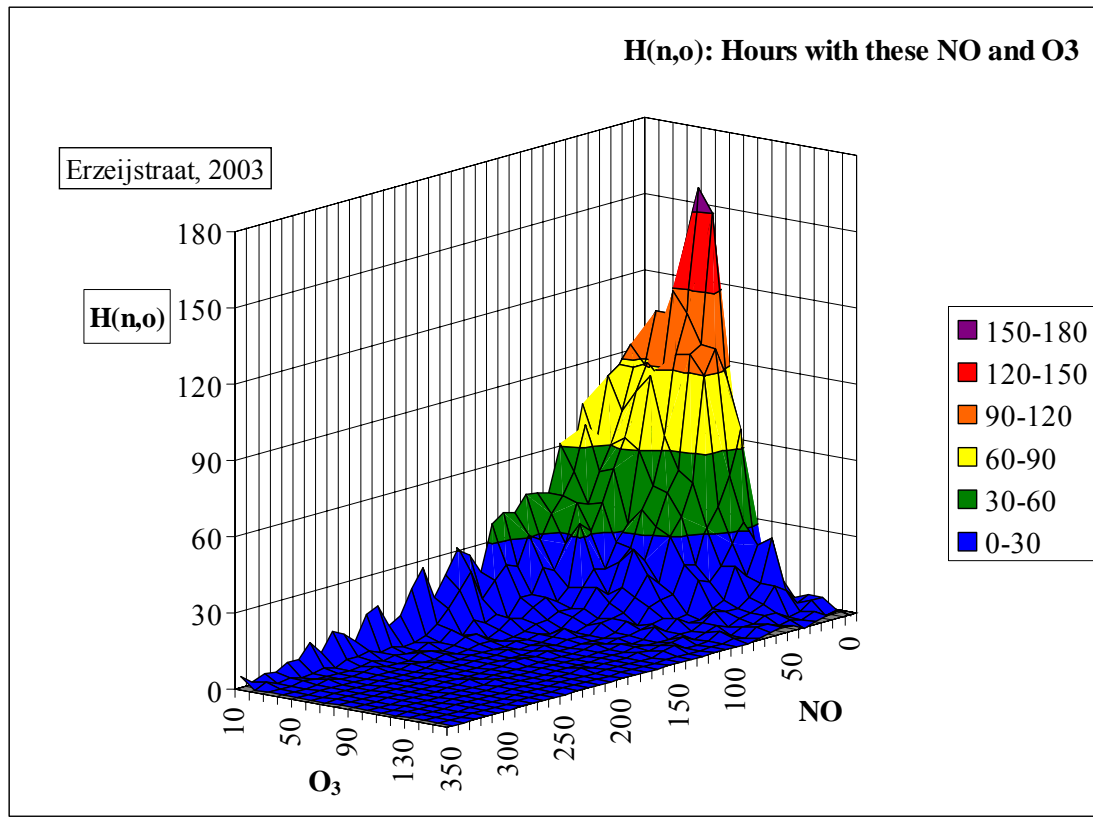


Figure A1-2 Distribution of the number of hours in the Erzeijstraat in 2003 with specific values for the O₃ and NO contribution.

With $H(n, o)$, the yearly average conversion contribution can also be rewritten as a sum over all possible values of the NO and O₃:

$$\overline{g(n, o)} = g(\bar{n}, \bar{o}) \frac{1}{M} \sum_{j=NO_x} \sum_{k=ozone} H(n_j, o_k) \beta(n_j) \cdot \gamma(o_k) \quad (A1-13)$$

From the above it is clear that the correction factor depends on a number of factors, with $\gamma(o_k)$ taking into account the O₃ dependency of the correction, a function $\beta(n_j)$ taking into account the NO (or NO_x) dependency of the correction and a function $\alpha(n_j, o_k)$ taking into account possible deficiencies of the underlying model which, in this case, is given by relation (4). The distribution $H(n, o)$ will vary somewhat from year to year, mainly due to meteorological and traffic variations. We can write Equation (A1-13) as

$$\overline{g(n, o)} = g(\bar{n}, \bar{o}) \cdot \bar{\chi} \quad (A1-14)$$

with:

$$\bar{\chi} = \frac{1}{M} \sum_j \sum_k H(n_j, o_k) \cdot \beta(n_j) \cdot \gamma(o_k) \quad (\text{A1-15})$$

Using the definitions

$$\frac{1}{M} \sum_j \sum_k H_{jk} = 1, \quad \bar{\beta} = \frac{1}{M} \sum_j \sum_k H_{jk} \cdot \beta_j, \quad \bar{\gamma} = \frac{1}{M} \sum_j \sum_k H_{jk} \cdot \gamma_k \quad (\text{A1-16})$$

the above can also be written as:

$$\bar{\chi} = \bar{\beta} + \overline{\delta\beta_i \cdot \delta\gamma_i} = \frac{1}{M} \sum_j \sum_k H_{jk} \cdot \beta_j + \frac{1}{M} \sum_i \sum_k H_{jk} \cdot \delta\beta_i \cdot \delta\gamma_i \quad (\text{A1-17})$$

The factor $\bar{\chi}$ is equal to the ratio of the yearly averaged amount of converted NO₂ calculated from individual hourly concentrations and the yearly averaged amount of converted NO₂ calculated from yearly averaged NO and O₃ concentrations, assuming the conversion model to be correct. The factor $\bar{\chi}$ depends on the structure of the conversion model (A1-6) and on the distribution of – and correlation between – the NO contributions and O₃ concentrations.

For the example of the Erzeijstraat in 2003, we find the following correlation:

$$\bar{\beta} = 0.79, \quad \overline{\delta\beta_i \cdot \delta\gamma_i} = -0.13, \quad \frac{\overline{\delta\beta_i \cdot \delta\gamma_i}}{\bar{\beta}} = -0.163, \quad \bar{\beta} + \overline{\delta\beta_i \cdot \delta\gamma_i} = 0.66.$$

In the Dutch model SRM-1, a fitted value of 0.6 is used for the expression $\bar{\beta} + \overline{\delta\beta_i \cdot \delta\gamma_i}$.

The concentration contribution is usually defined as the difference between the concentration in the street and the concentration at a nearby city background location. The theory still applies if, for some reason, a city background concentration is not available and a large-scale regional concentration is used; however the values for $H(n, o)$ and, therefore, also for $\bar{\chi}$ will then be different.

Model performance

So far we have assumed that (hourly) model results are in good agreement with reality – i.e. with field measurements. In the case of a flawed model, however, (systematic) differences between the calculated and measured concentrations may occur. We therefore define an hourly function $\alpha_t()$ that is the ratio between the measured and calculated NO₂ conversion concentration contribution. The function $\alpha_t()$ may depend on many parameters or conditions. With this function included in the calculations, we can write the expression for the yearly averaged NO₂ conversion concentration as:

$$\overline{g(n,o)} = g(\overline{n},\overline{o}) \frac{1}{M} \sum_i \alpha(f_i, n_i, \text{nox}_{bg,i}, \dots) \cdot \beta(n_i) \cdot \gamma(o_i) \quad (\text{A1-18})$$

The summation runs over all hours. Assuming $\alpha(\)$ depends mainly on n_j and o_k , we can rewrite Equation (A1-18) as a sum over all possible NO and O₃ concentrations:

$$\overline{g(n,o)} = g(\overline{n},\overline{o}) \frac{1}{M} \sum_j \sum_k H(n_j, o_k) \cdot \alpha(n_j, o_k) \cdot \beta(n_j) \cdot \gamma(o_k) \quad (\text{A1-19})$$

The value of $\overline{\chi}$ does not depend on whether the conversion model is correct or not. In the case where the model for calculating the hourly amount of converted NO₂ is not (fully) correct for all hours, we can write a similar relation for the correction factor $\overline{\theta}$:

$$\overline{\theta} = \frac{1}{M} \sum_{j=\text{nox}} \left(\sum_{k=\text{ozon}} H(n_j, o_k) \cdot \alpha(n_j, o_k) \cdot \beta(n_j) \cdot \gamma(o_k) \right) \quad (\text{A1-20})$$

We also define a correction factor for model deficiencies $\overline{\alpha}$:

$$\overline{\alpha} = \frac{\overline{\theta}}{\overline{\chi}}. \quad (\text{A1-21})$$

The values of $\alpha(n_j, o_k)$ are difficult to estimate and will depend on many factors. For example, the NO_x background concentration does not influence the result of the conversion function (A1-6), whereas calculations with the chemistry package of the OSPM do indicate an influence. These mechanisms may result in the values of $\alpha(n, o)$ and, therefore, the values of $\overline{\theta}$ and $\overline{\alpha}$ to vary both in time and location. Because the distribution of values $\alpha(n_j, o_k)$ is not known, it is not possible to simplify the above summations as was done in the previous chapter.

Comparison with measurements

The average correction factors $\overline{\theta}$, $\overline{\chi}$ and $\overline{\alpha}$ can be calculated using the relations derived above. However, the numerical values of the correction factors can also be determined from a direct comparison of calculated and measured concentrations. Let us assume sets of measured and calculated hourly NO₂ conversion concentration contributions $\{c_i^m\}$ and $\{c_i^c\}$, respectively. As already mentioned, we define the conversion concentration here as the amount of NO₂ that was converted from NO into NO₂ in a photolytic reaction in the presence of O₃. The measured NO₂ conversion concentration contribution is defined as the NO₂ concentration contribution minus the assumed fraction of directly emitted NO₂ multiplied by the NO_x concentration contribution. The values of \overline{n} and \overline{o} are calculated

from the hourly data. Using the above definitions we can determine the measured value of $\bar{\chi}$ from the ratio of averaged hourly values (denoted with the subscript “h”):

$$\bar{\chi}_h = \frac{\overline{c^c}}{g(\overline{n}, \overline{o})}. \quad (\text{A1-22})$$

Similarly, for the measured value of $\bar{\theta}$:

$$\bar{\theta}_h = \frac{\overline{c^m}}{g(\overline{n}, \overline{o})}. \quad (\text{A1-23})$$

and:

$$\bar{\alpha}_h = \frac{\overline{c^m}}{\overline{c^c}}. \quad (\text{A1-24})$$

A complication in this analysis is the exact value of the fraction of directly emitted NO₂, which is denoted by f . The uncertainty in this fraction influences both the calculated and the measured conversion concentration contribution. A more detailed analysis is presented in Appendix 3. With the distribution $H(n, o)$ determined for the Erzeijstraat in 2003 and a value of $f=0.08$, we can calculate $\bar{\chi}$ according to Equation (A1-15), obtaining a value of 0.66. Direct calculation of Equation (A1-22) from the available hourly data gives the same value. The value of $\bar{\chi}$ obtained from Equation (A1-22) is not sensitive to the value of the directly emitted NO₂, while the value of $\bar{\alpha}_h$ obtained from Equation (A1-24) is quite sensitive to the value of the directly emitted NO₂.

The conversion model (A1-6) is not perfect, and the calculated amount of converted NO₂ as a function of the available O₃ differs slightly from the measured amount. Figure A1-3 shows both relations. Figure A1-4 shows the ratio of the measured and calculated concentrations.

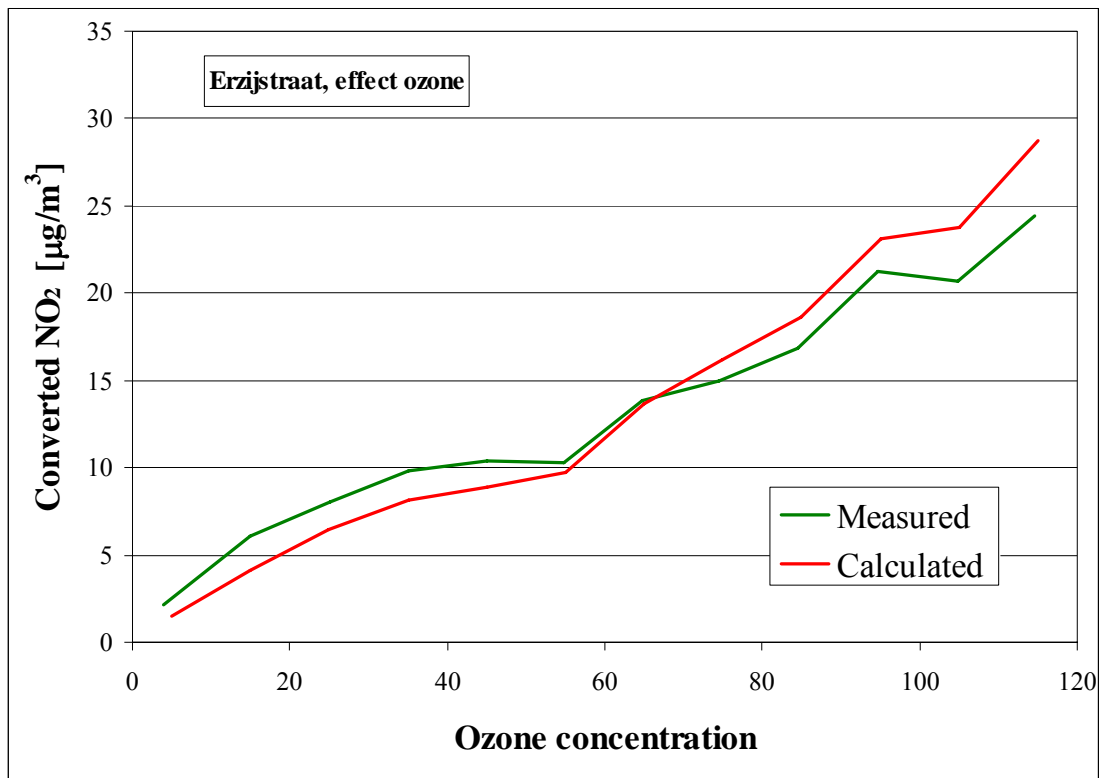


Figure A1-3 Calculated and measured NO₂ conversion concentration contributions as a function of available O₃.

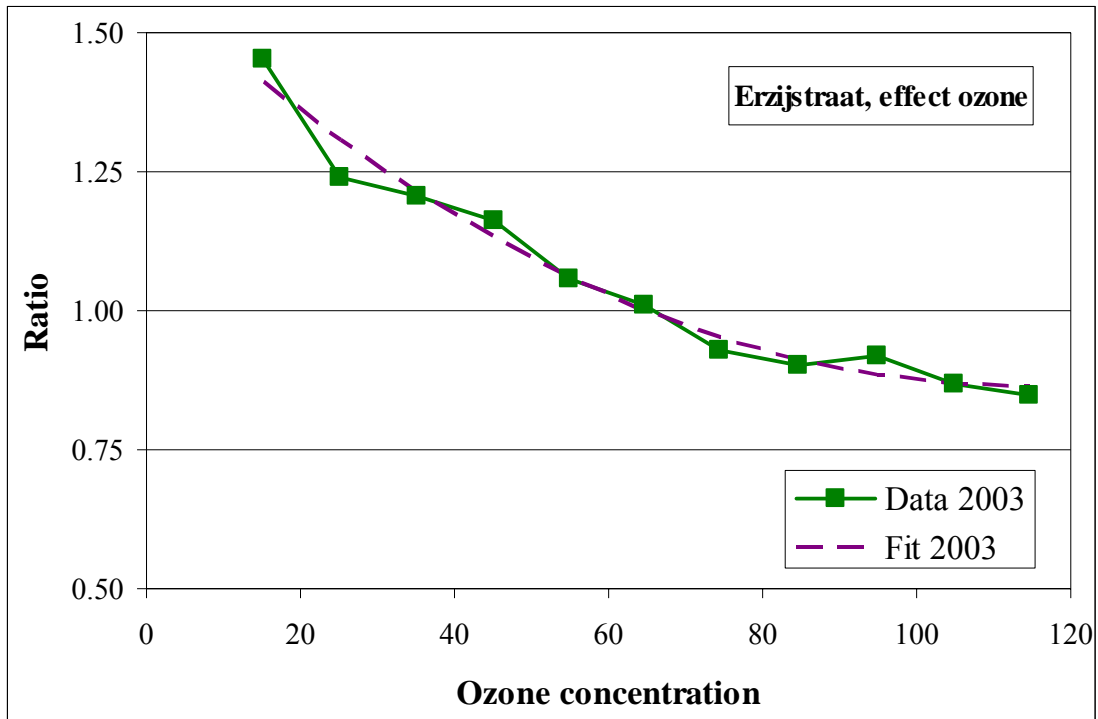


Figure A1-4 Ozone-dependent ratio of calculated and measured converted NO₂

The model deviations seem to be dependent mainly on the O₃ concentrations, and the amount of NO due to traffic has only a minor effect. Therefore, only O₃ is used in calculating the function $\alpha(n, o)$. For ease of use in evaluating Equation (A1-16) the data shown in Figure A1-4 have been fitted:

$$\alpha(n, o) = 1.59 + 12.7 \cdot 10^{-3} o + 5.56 \cdot 10^{-5} o^2 \quad (\text{A1-25})$$

Using Equation (A1-25), we can evaluate the correction factor $\bar{\theta}$ shown in (A1-20), obtaining a value of 0.71, leading to a value of 1.08 for $\bar{\alpha}$. From the measured and calculated data we obtain $\bar{\theta}_h = 0.70$ and $\bar{\alpha}_h = 1.06$, which are in good agreement. Both values for $\bar{\theta}$ and $\bar{\theta}_h$ must be compared to the empirical factor being used in the Dutch standard calculation model 1 (SRM-1), which is 0.6. Using MATLAB, we can determine the values for $\bar{\chi}_h$, $\bar{\theta}_h$ and $\bar{\alpha}_h$ using Equations (A1-22)–(A1-24) from the data for the period 1996–2003. The results are plotted in Figure A1-5. In these analyses values for the directly emitted NO₂ ranging from 5% in 1996 up to 8% in 2003 have been used. These values were determined in a separate study by the RIVM, the results of which will be published in 2008. The value for 2003 has also been verified in a separate O_x/NO_x analysis (see Appendix 5).

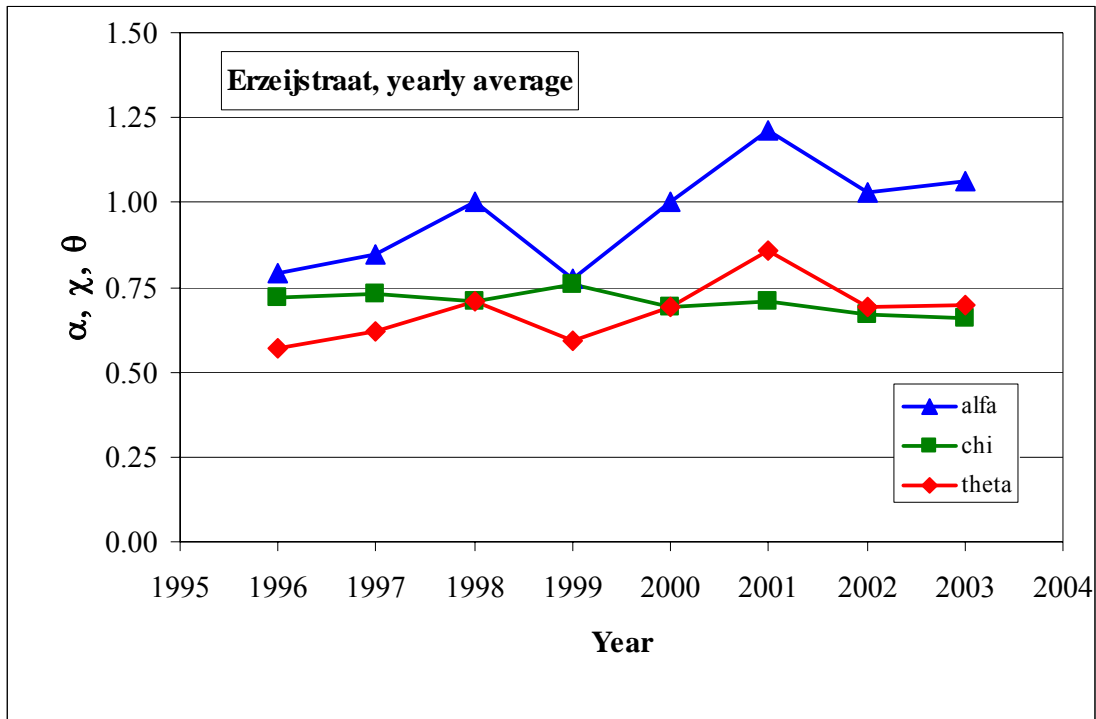


Figure A1-5 Values for $\bar{\chi}_h$, $\bar{\theta}_h$ and $\bar{\alpha}_h$ for the period 1996–2003.

The value of $\bar{\chi}_h$ varies only slightly from year to year, with values ranging from 0.66 to 0.77. The value of $\bar{\theta}_h$, however, varies substantially more, with values between 0.57 and 0.86. As already mentioned, these values must be compared to the value of 0.6 being used in SRM-1. The value of $\bar{\alpha}_h$ varies between 0.78 and 1.21.

Averaging within wind sectors

In a number of situations the Dutch dispersion models calculate the concentration contributions for a number (usually 12) of wind directions or wind sectors. The yearly averaged concentration is then obtained from a weighted average of the sectors. The analysis of the non-linearity can be extended for the case of discrete sectors. Within each sector the variation in O_3 concentrations is smaller than that over the full 360 degrees, as is the variation in NO_x contributions; the correlation between the NO_x and O_3 concentrations will also be different. Therefore, the results of this analysis will differ from those derived using the equations mentioned in the preceding section. The expressions (A1-15) and (A1-20) can be evaluated for only those hours where the hourly averaged wind is within specific sectors.

Urban situations

As an example of the above, let us take two sectors of the Erzeijstraat: (1) 120–150 degrees, with a large NO_x contribution from the traffic in the street; (2) 270–300 degrees, with a small contribution. The NO_x concentration distributions differ substantially, as shown in Figure A1-6.

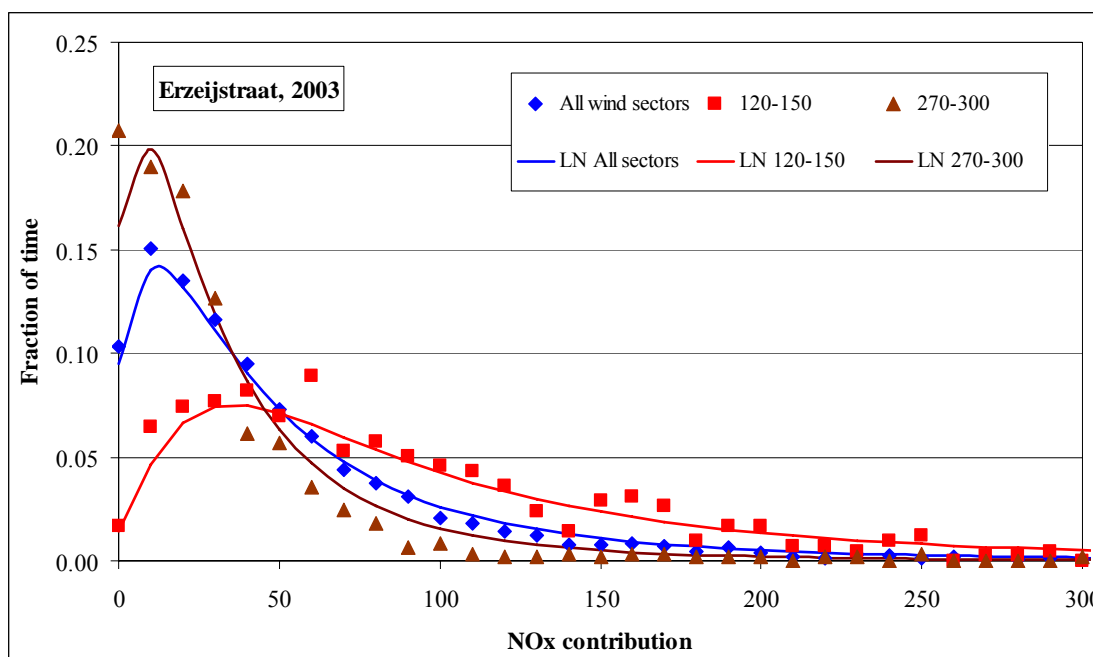


Figure A1-6 Distribution of NO_x concentration contributions measured in the Erzeijstraat in 2003 for all data and for two wind sectors. The curves labelled 'LN' are lognormal fits to the data.

The values of the correction factors determined for the three cases using relations (A1-15), (A1-20) and (A1-21) are shown in Table A1-1.

Table A1-1 Values for the factors $\bar{\alpha}$, $\bar{\chi}$ en $\bar{\theta}$ in the Erzeijstraat in 2003.

SECTOR	FORMULAE (A1-15), (A1-20), (A1-21)			FORMULAE (A1-22)–(A1-24)		
	$\bar{\chi}$	$\bar{\theta}$	$\bar{\alpha}$	$\bar{\chi}$	$\bar{\theta}$	$\bar{\alpha}$
0–360 degrees	0.66	0.71	1.08	0.72	0.78	1.08
120–150 degrees	0.74	0.87	1.18	0.73	0.87	1.19
270–300 degrees	0.69	0.69	1.00	0.67	0.65	0.97

The factors can also be determined directly from the measured and calculated hourly concentrations:

$$\overline{\chi_{S h}} = \frac{\overline{c_S^c}}{g_S(\overline{n_S}, \overline{o_S})}. \quad (\text{A1-26})$$

The bar and subscript “S” indicate that the averaging was performed for values within one wind sector. Furthermore:

$$\overline{\theta_{S h}} = \frac{\overline{c_S^m}}{g_S(\overline{n_S}, \overline{o_S})} \quad (\text{A1-27})$$

and

$$\overline{\alpha_{S h}} = \frac{\overline{c_S^m}}{\overline{c_S^c}} = \frac{\overline{\theta_{S h}}}{\overline{\chi_{S h}}}. \quad (\text{A1-28})$$

The values of $\overline{\theta_{S h}}$, $\overline{\alpha_{S h}}$ and $\overline{\chi_{S h}}$ have also been determined from the available experimental data over the period 1996–2003. The wind rose of values for the Erzeijstraat in 2003, using the meteo data from the location Schiphol, is shown in Figure A1-7. The resulting factors $\overline{\theta_{S h}}$, $\overline{\alpha_{S h}}$ and $\overline{\chi_{S h}}$ are also shown in Table A1-1. The factors are either a weighted average over sector values or averaged over the full wind rose directly; however, in the case of a full wind rose, the method used produces different results.

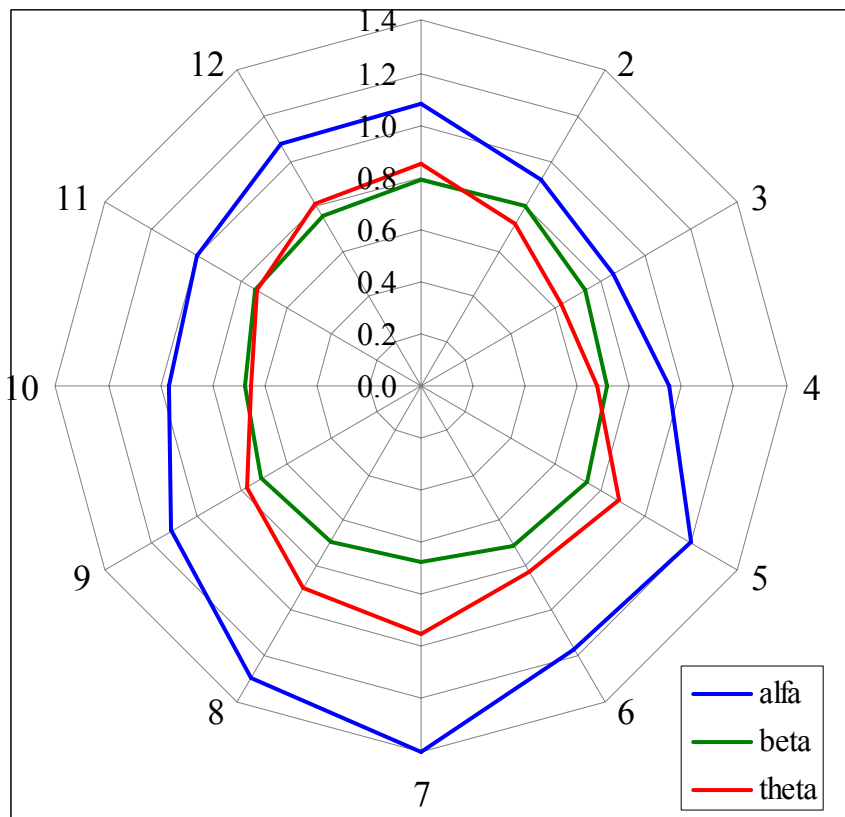


Figure A1-7 Values for $\overline{\theta}_{S_h}$, $\overline{\alpha}_{S_h}$ and $\overline{\chi}_{S_h}$ as a function of the wind direction in the Erzeijstraat for 2003.

The value of $\overline{\chi}_{S_h}$ seems to be quite independent of the angle, whereas the value of $\overline{\alpha}_{S_h}$ changes substantially with the angle. This variation suggests there may be several mechanisms at play that have not been modelled.

The wind rose-averaged values are presented in Figure A1-8 for the period 1996–2003.

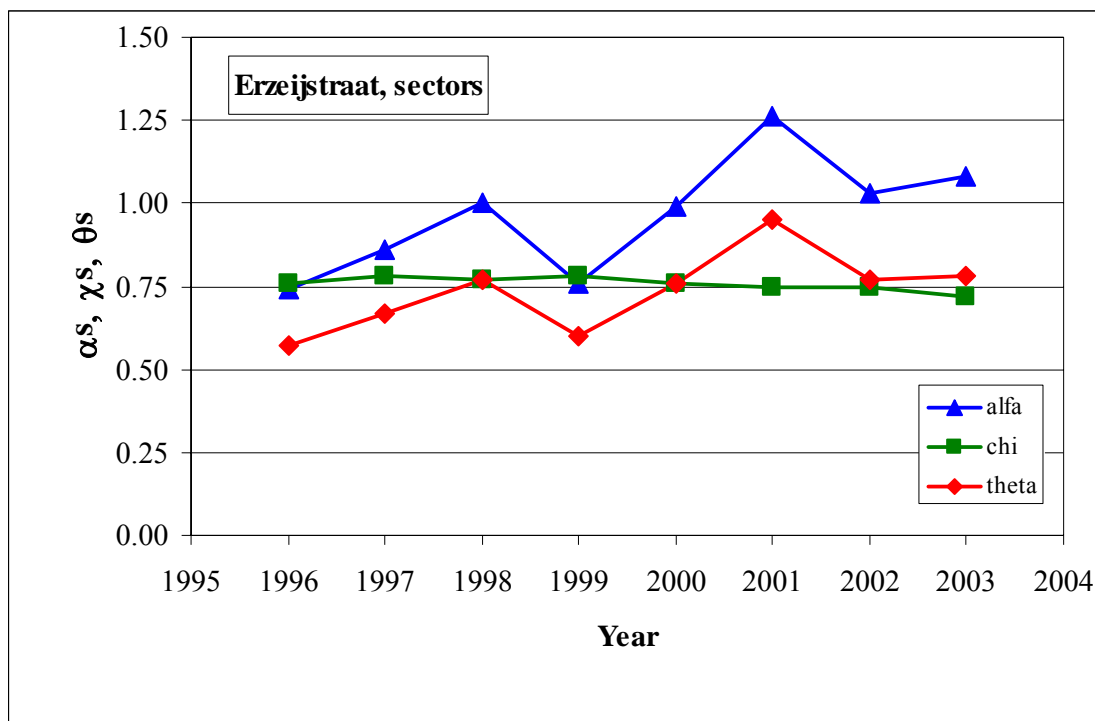


Figure A1-8 Values for $\overline{\theta_{S_h}}$, $\overline{\alpha_{S_h}}$ and $\overline{\chi_{S_h}}$ in the Erzeijstraat in the period 1996–2003.

Rural situations

A similar analysis was performed for the rural location of the Breukelen measuring station LML641, which was situated directly next to the A2 motorway. Only corrections for the wind rose are relevant for measurements made next to a highway. In a street canyon the traffic emissions can, to some extent, be measured for almost all wind directions. In an open field situation, however, traffic concentration contributions are only measured for roughly half of the wind directions. The distribution of NO_x concentration contributions, obtained by obtaining the difference in NO_x concentrations between LML641 and the background station LML633 (Zegveld), is shown in Figure A1-9.

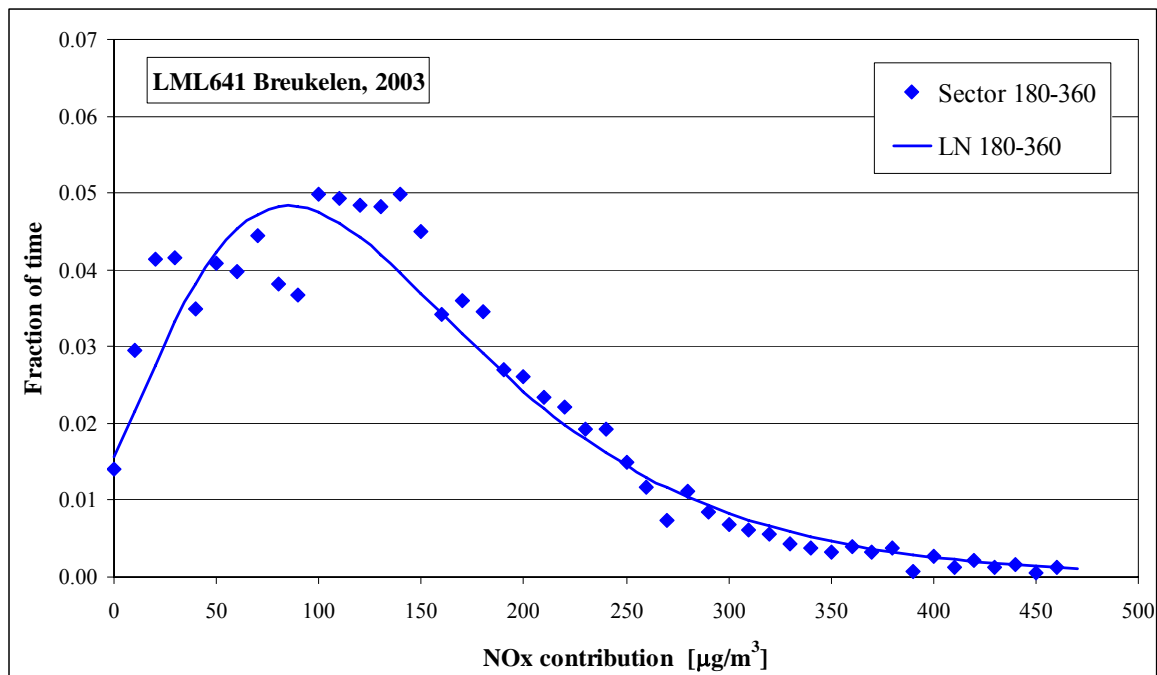


Figure A1-9 The distribution of NO_x concentration contributions at LML641, Breukelen.

A comparison of Figure A1-9 with Figure A1-1, which shows similar data for the street canyon situation, reveals a marked difference. The parameters of the lognormal distribution also shown in the figure are $\delta = 100$ (fixed), $\mu = 5.15$ and $\sigma = 0.56$.

An O_x/NO_x analysis shows that the fraction of directly emitted NO_2 by the traffic on the A2 motorway is 11%. The number of hours with specific NO concentration contributions and O_3 background concentrations in 2003 is shown in Figure A1-10.

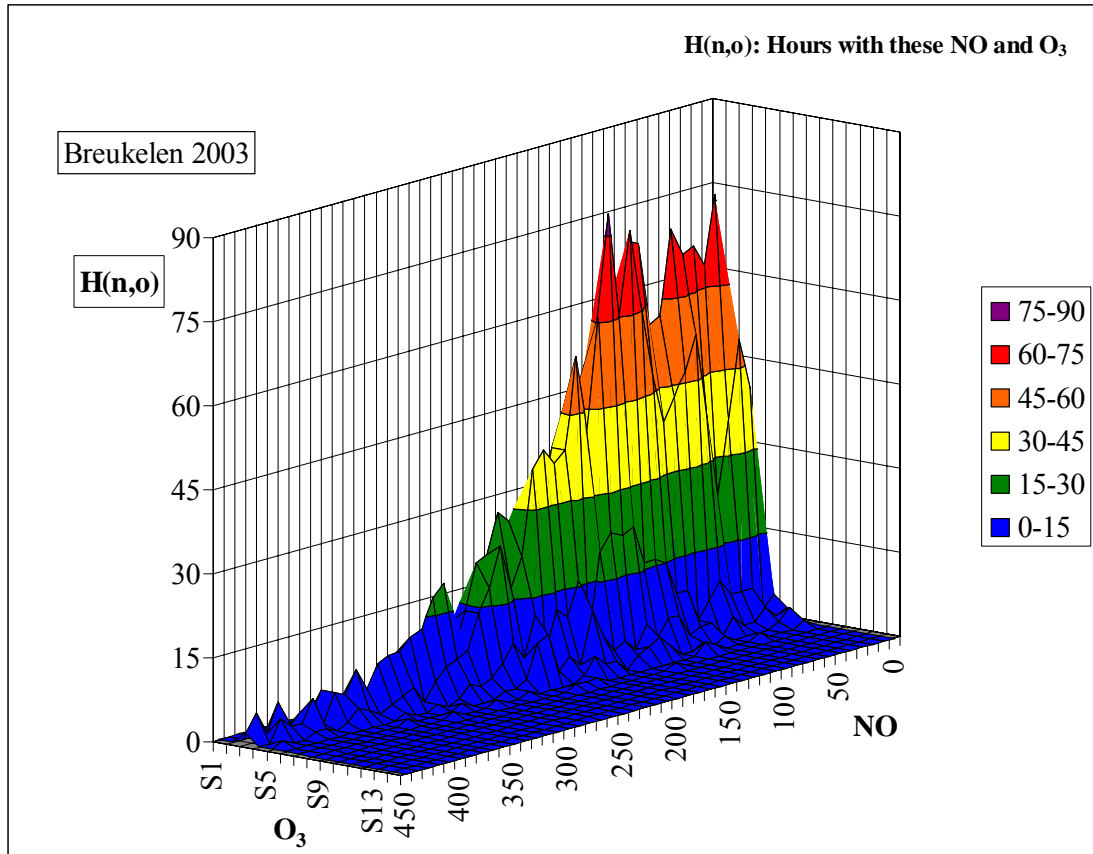


Figure A1-10 Distribution of the number of hours at the location Breukelen in 2003 with specific values for the O_3 and NO contribution.

The correction factor $\bar{\chi}$ (A1-15) can be determined using the distribution $H(n, o)$ shown in Figure A1-10 and expressions (A1-1) and (A1-9). This value is $\bar{\chi} = 0.83$. A direct comparison of calculated and measured NO_2 conversions using Equations (A1-22)–(A1-24) yields yearly average values of $\bar{\chi}_s = 0.88$, $\bar{\theta}_s = 0.76$ and $\bar{\alpha}_s = 0.87$. In this analysis the fraction of directly emitted NO_2 varies between 3% in 1996 and 16% in 2007. The values of $\bar{\alpha}_s$, $\bar{\chi}_s$ and $\bar{\theta}_s$ for the period 1996 – 2006 are plotted in Figure A1-11.

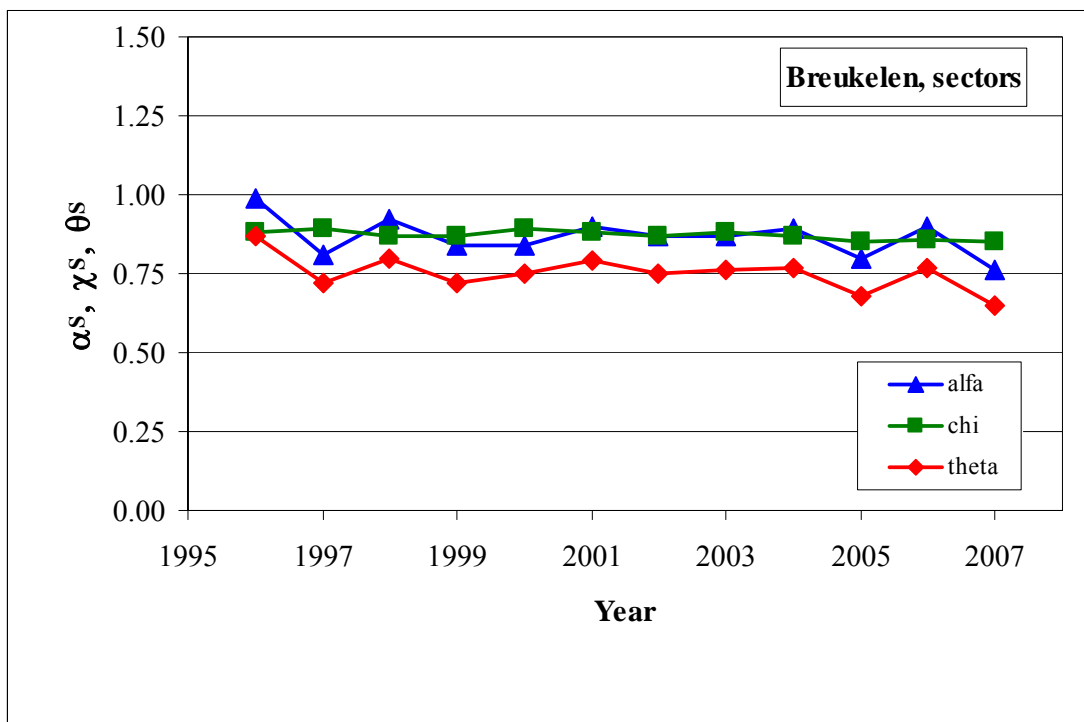


Figure A1-11 Values for $\overline{\theta}_s$, $\overline{\alpha}_s$ and $\overline{\chi}_s$ at the Breukelen location in the period 1996–2007.

The values are quite constant over the whole period. The value of $\overline{\theta}_s$ varies slightly, with an average value of 0.75; similarly, the value of $\overline{\alpha}_s$ varies slightly, with an average value of 0.87. The value of $\overline{\chi}_s$ is practically constant at 0.87.

It should be noted that the exact definition of the wind sectors participating in the averaging function influences to some extent the values obtained for $\overline{\alpha}_s$, $\overline{\chi}_s$ en $\overline{\theta}_s$.

Appendix 2 NO_x/NO₂ conversion in CAR; history

The CAR model was proposed by van den Hout and Baars (1988). It consists of a number of simple dispersion relations that can be used in schematic two-dimensional streets, which can be either street canyons or more open streets. Studies showed that NO_x contributions from traffic in the schematic streets had a simple structure. In open situations there was a NO_x contribution in approximately seven of twelve wind sectors, whereas next to a building there was a NO_x contribution in all wind sectors, as illustrated in Figure A2-1.

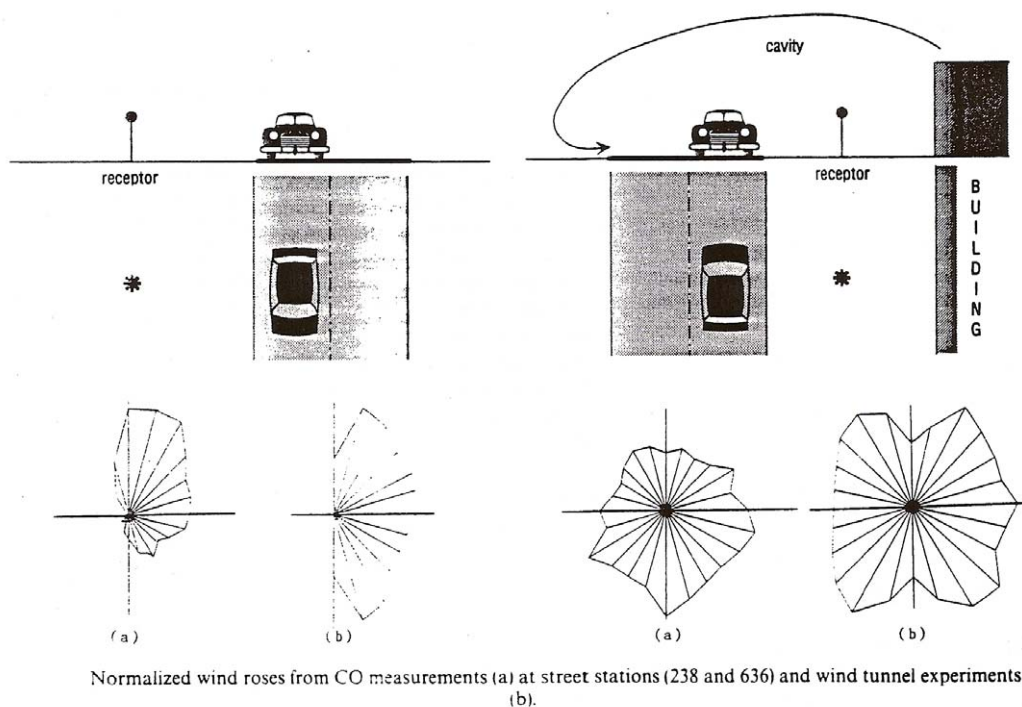


Figure A2-1 NO_x contributions for different street configurations (taken from Eerens et al., 1993).

The following relation between the yearly averaged NO_x and NO₂ concentrations was assumed by Van den Hout and Baars (1988):

$$\Delta NO_2 = 0.05 \Delta NO_x + f \cdot O_3 \cdot \frac{\Delta NO_x}{\Delta NO_x + 100} \quad (A2-1)$$

In this relation the fraction 0.05 is the amount of directly emitted NO₂, and the parameter *f* takes into account the fraction of the time that pollutants from the traffic can reach a receptor. Strictly speaking the NO_x contributions in the second term should be scaled by 0.95, this was neglected as this was

hardly relevant³ in 1988. The fraction was derived from a more general relation in which the NO_x/NO₂ conversion was weighted over 12 wind sectors, with the amounts of O₃ and NO_x dependent on the wind direction (ϑ):

$$\Delta NO_2(\vartheta) = 0.05 \Delta NO_x(\vartheta) + O_3(\vartheta) \cdot \frac{\Delta NO_x(\vartheta)}{\Delta NO_x(\vartheta) + 100} \quad (\text{A2-2})$$

In deriving (A2-1) from (A2-2), the amount of O₃ was assumed to be constant in all directions. Furthermore, for street canyon-like situations, it was also assumed that the amount of NO_x from the traffic has either a constant value N , for 7/12 of the time, or a value of zero, for 5/12 of the time, resulting in a yearly average of $\bar{N} = \frac{7}{12}N$. Applying these assumptions, relation (A2-2) can be rewritten for street canyon-like situations as:

$$\Delta NO_2 = 0.05 \bar{N} + \frac{7}{12} \cdot O_3 \cdot \frac{\bar{N}}{\bar{N} + \frac{12}{7} \cdot 100} \quad (\text{A2-3})$$

In the case that pollutants from the traffic can reach the receptor from all sides, we find:

$$\Delta NO_2 = 0.05 \bar{N} + O_3 \cdot \frac{\bar{N}}{\bar{N} + 100} \quad (\text{A2-4})$$

In their report, Van den Hout and Baars concluded that relation (A2-1) can be used with $f = 0.6$ (note that $7/12 = 0.58$) for street canyon-like situations and $f = 1.0$ in the case of pollutants from the traffic reaching the receptor from all sides. Comparing (A2-3) with (A2-1) we find that the denominator ($\bar{N} + 100$) should be replaced by ($\bar{N} + 171$). However, this was neglected.

In practice the idealized schematic wind rose of NO_x contributions does not occur in many situations. In addition, both the NO_x and O₃ concentrations may vary substantially in realistic situations. The value of $f = 1.0$ for situations in which pollutants from the traffic can reach the receptor from all sides has never been implemented in the CAR model. Consequently, $f = 0.6$ was used in all cases. In a later study by Eerens (1993), the values of K and f , then named β (not to be confused with the β as used in this report), were fitted to a limited data set. The value of β was kept at 0.6, and a value of 130 was obtained for K .

The value $K = 130$ was not used in CAR. Following an update in 1998 (Vissenberg, 1998), the value of $K = 300$ was used. Later, after yet another update (Teeuwisse, 2003), the value of $K = 100$ was used.

³ It should be noted that the focus on the exact values (up to the 2nd decimal) of concentrations only started around 2003.

The value of $\beta = 0.6$ has been kept in all versions of CAR. In an extensive recalibration of CAR (Wesseling, 2007), the values of $K = 100$ and $\beta = 0.6$ were kept.

Appendix 3 Sensitivities

As mentioned earlier in this report, the value of $\bar{\chi}$ depends on both the hourly correction factor $\beta(n_j)$ and the factor $\gamma(o_j)$. From the underlying definitions it is clear that none of the components of relation (22) depends directly on the value of the directly emitted fraction of NO₂. The value obtained for $\bar{\theta}$ and, therefore, the value obtained for $\bar{\alpha}$, are very sensitive to the assumed fraction of direct NO₂ emissions. The assumed amount of directly emitted NO₂ is subtracted from the measured NO₂ concentration contribution to obtain the amount of NO₂ converted from NO emitted by traffic. This measured conversion part is compared to the calculated conversion concentration contribution, which is defined as $(1-f)$ multiplied by the NO_x concentration contribution due to traffic. As a result, the uncertainty in the exact value of f reflects both on the measured and calculated values of the amount of converted NO₂.

Given measured NO₂ en NO_x concentration contributions C_{NO_2} en C_{NO_x} , the measured and modelled conversion contributions c_m and c_c are determined as:

$$c_m = C_{NO_2} - f \cdot C_{NO_x} \quad (A3-1)$$

$$c_c = O_3 \cdot \frac{(1-f) \cdot C_{NO_x}}{(1-f) \cdot C_{NO_x} + K} \quad (A3-2)$$

If the value of f increases, the value of c_m decreases and that of c_c increases. The parameter χ is defined as (see Appendix 1):

$$\chi = \frac{c_c}{g(\bar{n}, \bar{o})} = \frac{O_3 \cdot (1-f) \cdot C_{NO_x}}{(1-f) \cdot C_{NO_x} + K} \cdot \frac{(1-f) \cdot C_{NO_x} + K}{O_3 \cdot (1-f) \cdot C_{NO_x}} \quad (A3-3)e$$

This can be rewritten as:

$$\chi = \frac{c_c}{g(\bar{n}, \bar{o})} = \frac{O_3}{O_3} \cdot \frac{C_{NO_x}}{C_{NO_x}} \cdot \frac{\frac{C_{NO_x}}{C_{NO_x}} + \frac{K}{1-f}}{C_{NO_x} + \frac{K}{1-f}} \quad (A3-4)$$

It is clear from this relation that changes in f in the order of a few percentage points will scarcely have any effect at all on the value of χ .

The parameter α is defined as:

$$\alpha = \frac{c_m}{c_c} = \frac{((1-f) \cdot C_{NOx} + K) \cdot (C_{NO2} - f \cdot C_{NOx})}{O_3 \cdot (1-f) \cdot C_{NOx}} \quad (\text{A3-5})$$

An incorrect estimate for the value of f will therefore have a large effect on the value of α . For the Erzeijstraat in 2003, the effect of using different values for f on the resulting values of $\bar{\chi}$ and $\bar{\theta}$ is shown in Figure A3-1.

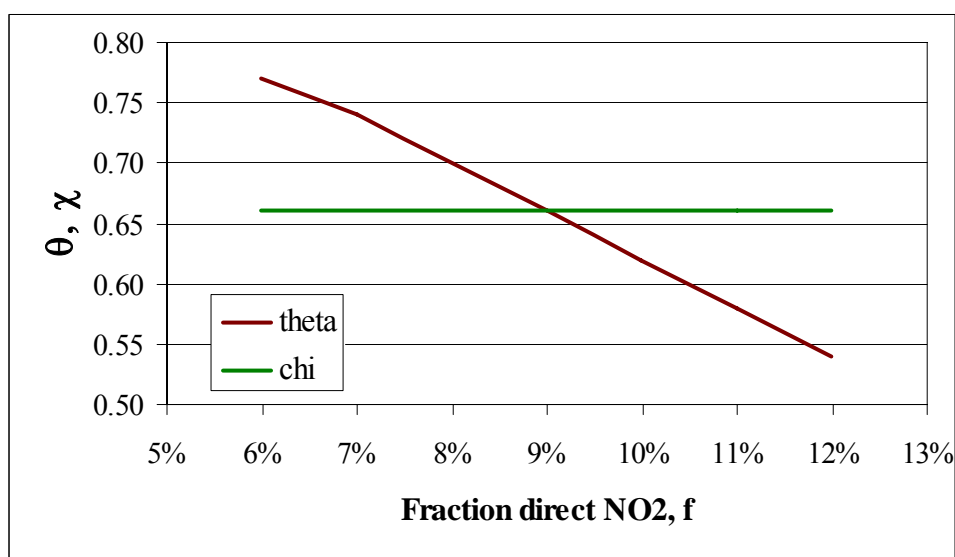


Figure A3-1 Values for the factors $\bar{\chi}$ en $\bar{\theta}$ as a function of the assumed fraction of directly emitted NO_2 , f .

The value of $\bar{\chi}$ is, as expected, constant (at 0.66) for all values of f , whereas the value of $\bar{\theta}$ changes substantially. Consequently, the value of $\bar{\alpha}$ changes, as shown in Figure A3-2.

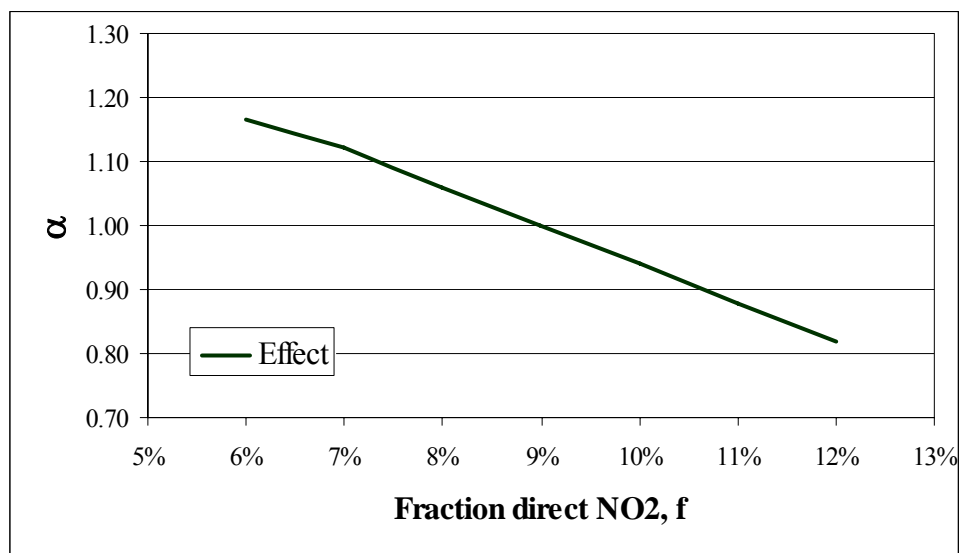


Figure A3-2 Variation in the value of $\bar{\alpha}$ as a function of the assumed fraction of directly emitted NO₂, f .

At a value of $f = 9\%$, the average model deviation, as expressed by $\bar{\alpha}$, is almost unity, which means that the measured and calculated concentrations do not differ. However, this does not signify that the model is correct, as there can be several compensating deficiencies. The RIVM will be carrying out further research in this area in 2008.

Appendix 4 Calibration of SRM-1

In 2007 the then last implementation of the SRM-1 was calibrated using field measurements of the RIVM (Wesseling and Sauter, 2007). First, the basic dispersion was calibrated by comparing measured and calculated NO_x and CO concentration contributions from the traffic. Next, the NO_x/NO₂ conversion was checked using the standard notation and formula of SRM-1:

$$\Delta NO_2 = f \Delta NO_x + \beta \cdot O_3 \cdot \frac{(1-f) \Delta NO_x}{(1-f) \Delta NO_x + 100} \quad (A4-1)$$

with f the fraction of directly emitted NO₂ and β the standard scaling of the photolytic conversion part, with a value of 0.60. For calibration tests, first NO_x contributions were determined by taking the difference between measured total NO_x concentrations and the NO_x background. Similarly, the NO₂ contributions were determined. Using relation (A4-1), NO_x contributions were calculated from the ‘measured’ NO_x contributions. The results, taken from the report, are shown in Figure A4-1.

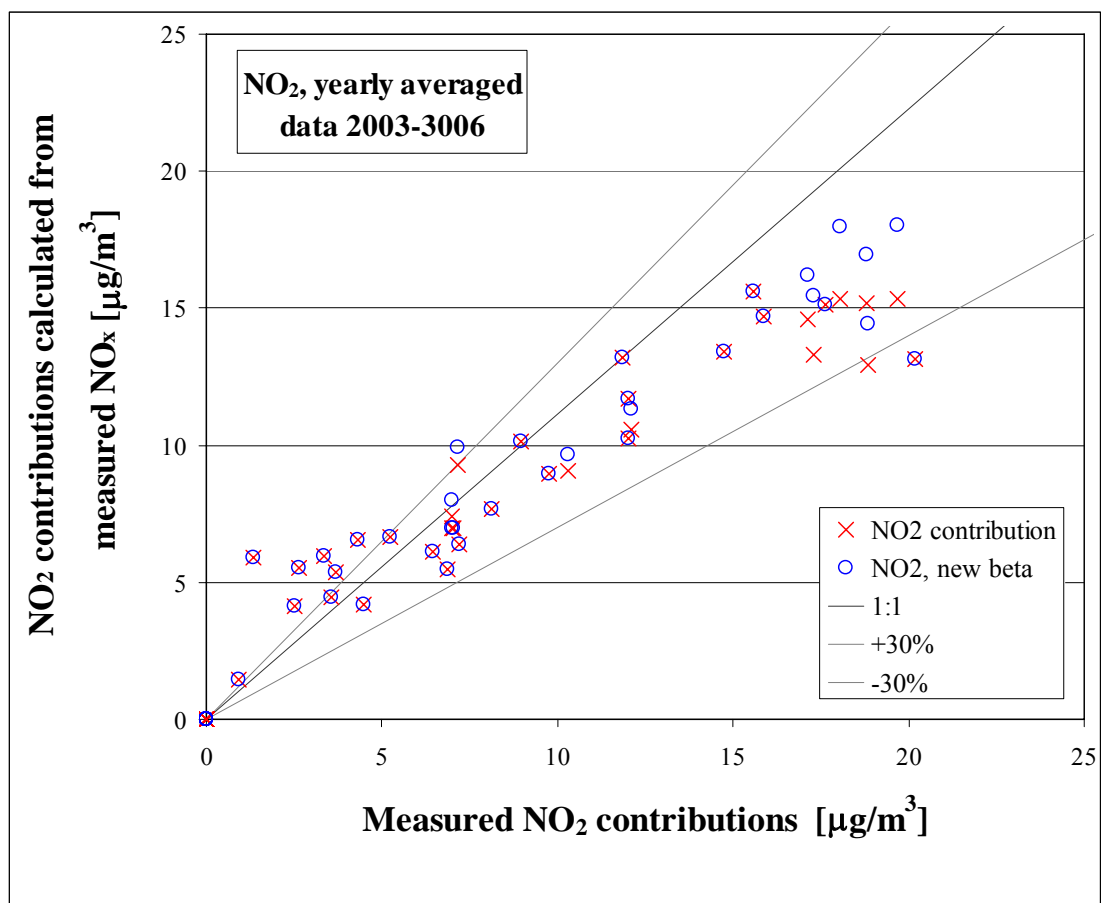


Figure A4-1 Comparison of measured and calculated NO₂ contributions as found in a previous study.

The original comparison of measured and calculated NO₂ contributions is shown using the red crosses. Overall, the agreement is quite satisfactory; only at high values of the NO₂ contributions the calculations seem to systematically underestimate the measured contributions. These data are from the stations in Nijmegen (Graafseweg) and Groningen (Europaweg).

From the present study estimates are available for the correct values of β at the Erzeijstraat, Graafseweg and Europaweg. For the period 2003-2006 the average values are 0.68, 0.75 and 0.80. Using these values in relation (A4-1), instead of the standard value of 0.60, results in higher NO₂ contributions. The results are also shown in Figure A4-1 with the blue circles. Especially at higher values of the NO₂ contributions there is a significant improvement of the agreement between measured and calculated NO₂ contributions. The increase in β for the Erzeijstraat leads to a slightly worse agreement at lower values of the NO₂ contributions.

Appendix 5 The amount of directly emitted NO₂

A simple and robust approach to determining the amount of directly emitted NO₂ is to plot the measured amount of OX \equiv NO₂ + O₃ as a function of the measured amount of NO_x (Carslaw and Beevers, 2004). The amount of OX at a location is independent of the NO_x/NO₂ conversion, as during the photolytic reaction oxygen atoms change from a O₃ molecule to a NO molecule. However, the amount of NO₂ directly emitted by local traffic comes on top of the ambient OX. In a plot of the amount of OX as a function of the amount of NO_x, the slope of the fit is therefore equal to the fraction of directly emitted NO₂. The plot of the O_x in the Erzeijstraat minus the OX at the background location in 2003 is shown in Figure A5-1. The fraction of directly emitted NO₂, determined using an orthogonal least squares fit to the data is 8%.

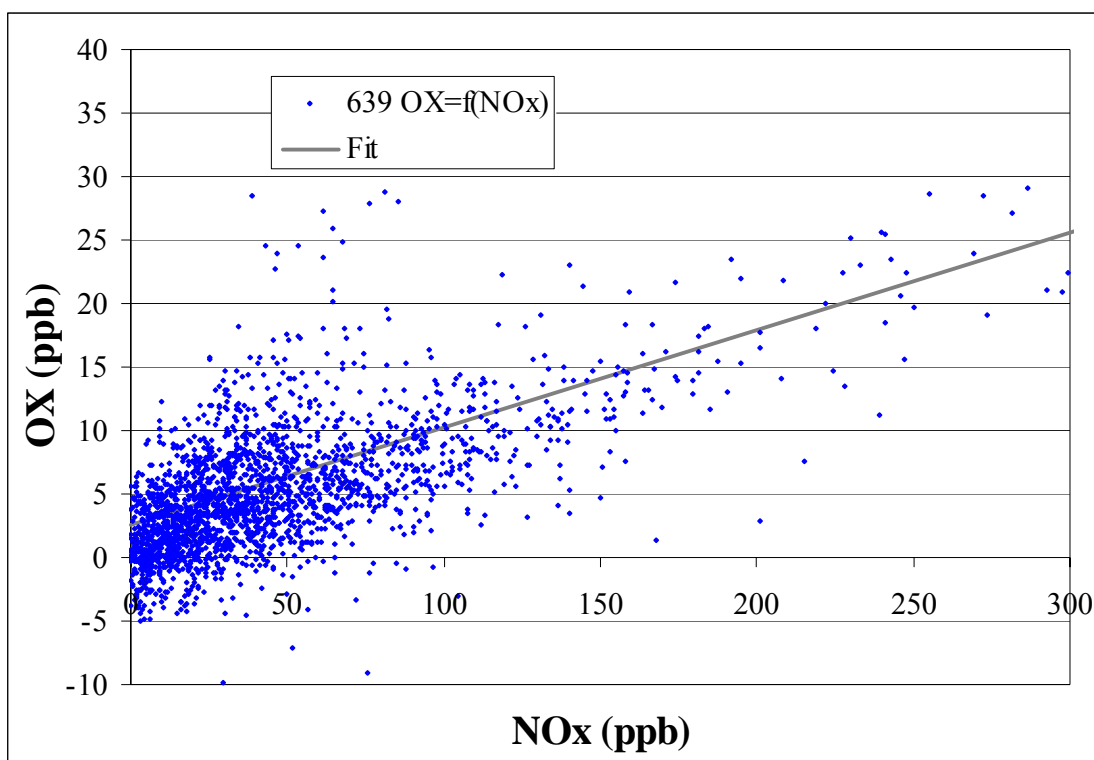


Figure A5-1 Measured OX as a function of the measured NO_x in the Erzeijstraat in 2003.