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TNO report

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N_2O-emission of HD vehicles

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Summary

N_2O is known to be a greenhouse gas with a high global warming potential, approximately 296 times higher than that of CO_2 [11]. In road vehicles N_2O is mostly formed by reactions in the exhaust catalyst. The IPCC (Intergovernmental Panel on Climate Change) uses emission factors from research performed in the late 1980's and early 1990's to calculate the contribution of road traffic to the global emission of N_2O. However, in the last decades much has changed with respect to vehicle technology. Furthermore, the currently available N_2O-emission factors for Heavy Duty (HD) vehicles have been extrapolated from the Light Duty (LD) emission factors by an assumed correlation with NO_x-emissions. Because of the high global warming potential, a clear need existed to derive reliable emission factors for N_2O that reflect the past, present and expected future contribution from traffic (the object period is defined as 1988 until 2010). A measuring programme of substantial size and diversity in vehicle technologies was considered far more relevant than a theoretical approach based on literature.

Within the framework of the ROB programme (ROB = Reductie Overige Broeikasgassen: reduction of other greenhouse gases), TNO Automotive (in co-operation with TNO MEP) has performed a research project for the Dutch Ministry of VROM -responsible for national environmental issues- to address among other things the following questions:

- What are the typical values for N_2O-emission from HD vehicles (ranging from pre-Euro 1 to Euro 5 technology)?
- What is known on the mechanisms of N_2O-formation, and can these help to understand the test results?
- Is there some kind of relation between N_2O- and NO_x-emissions?
- Is there a need to take policy measures against N_2O being emitted from HD vehicles?

The exhaust gas of a diesel engine contains some hydrocarbons and CO but mainly NO_x and particulate matter. Just as observed for gasoline engines, the N_2O-formation in the combustion chamber is generally rather low. However, N_2O might be emitted when the exhaust gas is treated with a catalyst. The combination of a relative low exhaust gas temperature and the specific active metals used in e.g. particulate filtration or the catalytic reduction of NO_x might cause N_2O-formation similarly to N_2O-formation during start-up over three-way catalysts in gasoline cars. Therefore, special interest was paid to vehicles with exhaust gas after-treatment devices, such as urea SCR-deNOx systems and CRT filters. These systems are likely to be applied on HD vehicles that have to apply for the Euro 4 standard and beyond.

In order to cover the full range of engine technologies used within the period from 1988 to 2010, a measurement programme consisting of the following vehicle types was set up:

- 3 Euro 1 vehicles
- 29 Euro 3 vehicles
- 2 demonstrator vehicles with experimental SCRdeNOx system
- 1demonstrator vehicle with experimental EGR system and a CRT filter
- 5 Euro 2 busses with CRT filter
- 2 CNG vehicles (one lean-burn and one stoichiometric engine)

Basically, the test comprises a simulated ESC 13-mode test on a steady-state chassis dynamometer. The method to simulate stationary tests on engines in vehicles has been

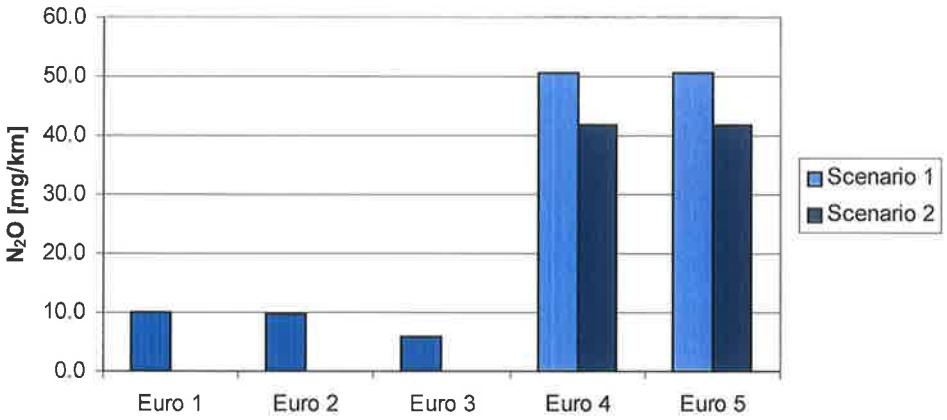
developed at TNO for the purpose of In-Use Compliance testing of trucks. For the Euro 1 and 2 vehicles the conventional ECE R49 13-mode test was used, while for Euro 3 the ESC test was performed. During the 13 modes, the N_2O-concentrations were measured continuously, including the transitions from one mode to the next, to provide insight into the transient N_2O-emissions. Apart from N_2O, also the regulated emission components were measured (CO, HC, NO_x, and PM) in order to assess the general (maintenance) condition of the engine, and to search for a possible correlation between NO_x and N_2O.
Apart from some troubles with CRT filters for high load parts of the testcycles, no testing problems were encountered.

For some of the vehicles that were tested, an additional test was performed with a cold engine. 'Cold' means that the oil and cooling liquid temperatures are at 22 °C when the test is started, while in a 'hot' test the engine has been given sufficient time to let the temperatures stabilise at a specified engine load.
N_2O-emission in vehicles with after-treatment systems was measured both up- and downstream of these systems to observe the difference in N_2O-concentration. Besides N_2O, the NH_3-emission was also screened for the two vehicles with a SCRdeNOx system.
In general, the N_2O-emissions of all test vehicles proved to be on a rather low level, in some cases even hardly above the minimum detection level of the measurement set-up. N_2O-emissions in tests performed after a cold engine start were of the same level as emissions after a hot start.
Taking the Global Warming Potential factor for N_2O into account (296 according to the IPCC [11]), the equivalent CO_2-emissions can be summarised as follows:

- Euro 1, 2 and 3 vehicles with conventional engine technology: < 3 g/kWh
- Euro 2 buses with CRT filter: 3 to 6 g/kWh
- Euro 2 CNG vehicles: <3 g/kWh (lean-burn) or <6 g/kWh (stoichiometric)
- Demonstrator vehicles with SCRdeNOx after-treatment systems: 9 to 21 g/kWh
- Demonstrator vehicle with EGR and CRT filter: <3 g/kWh

The CO_2-emission range for current HD engines over a 13-mode test is 630 to 720 g/kWh. This means that the maximum contribution of N_2O to the greenhouse effect for future HD vehicles equipped with SCRdeNOx after-treatment (in percentage of the CO_2 contribution) is not more than 3.5%. For the other engine technologies tested this percentage is even considerably lower (in the range of 0 to 1%).
Real-time measurements of the N_2O levels of the 2 vehicles with SCRdeNOx systems and the CRT vehicles did not show a straightforward correlation with the real-time NO_x-measurements apart from the obvious relation that N_2O-emissions are only high when NO_x-emissions are high. The reverse is not found to be true. It can therefore be stated that the relation of N_2O with engine-out NO_x is only of secondary nature and that NO_x-emission values cannot be used for modelling N_2O-emissions.
Another interesting finding is that for SCRdeNOx systems N_2O is formed in the lower temperature range, but not released until higher temperatures are reached. Therefore the N_2O-emissions during real-life driving situations will be very dependant of the temperature profile.
On the basis of the 13-mode emission results measured in this project, N_2O-emission factors have been calculated, estimating the emissions of HD vehicles under representative real-world driving conditions. The calculation is based on the method of Adapted Weighting Factors (without a transient correction), using a set of real-world driving cycles for HD vehicles. Emission factors for urban, rural and highway driving

with different load factors have been derived for Euro 1 to Euro 3 vehicles of 5 different classes and for vehicles with SCRdeNOx and CRT filters separately.
The figure below shows aggregate N_2O-emission factors, averaged over fleet composition and road types, for Euro 1 up to Euro 5 vehicles. For Euro 4 and 5 vehicles two scenarios are discerned with a different mix of exhaust after-treatment technologies assumed to be applied. It should be noted that due to aspects of both the measurement method and the calculation method the values in this figure should not be regarded as exact but rather as a good indication.



Real-life N_2O-emission factors for different HD engine technologies, for 2 scenario's (1 - 100% SCRdeNOx after-treatment, 2 – 80 % SCRdeNOx and 20% cooled EGR with CRT filter)

As this figure shows, N_2O-emissions of present-day trucks (Euro 1 to 3) are well below the value of 30 mg/km assumed by the IPCC. Beyond 2005, when exhaust after-treatment is expected to be used to meet the Euro 4 and 5 emission limits, the N_2O-emission of trucks and buses is expected to rise significantly to a value even higher than the IPCC value. However, expressed in CO_2-equivalents this value represents only 15 gCO_2/km at maximum, which is less than 2% of the direct CO_2-emission of HD vehicles (about 820 g/km if the same weighing is applied).
A rough indication of the national N_2O-emission by HD vehicles in the Netherlands showed that over the object period the absolute emission level would increase from 0.07 ktonne in 1988 to some 0.30 ktonne in 2010. In terms of CO_2-equivalents this means an increase from 21 to 87 ktonnes (for reference purpose: the total road traffic related CO_2-emission in the Netherlands over 2001 amounted to 32.0 Mtonne).
In this report, quite a number of inaccuracies and uncertainties related to the measurement set-up and the chosen calculation approach have been summed up. Consequently, the results obtained for the emission factors cannot be seen as an absolute fact. Within the boundary conditions of testing methods, analyser specifications, and availability of data on vehicles and driving conditions, the authors have tried to come up with the best representative results possible. Nevertheless, a large uncertainty margin needs to be taken into consideration, especially for the emission factors in the lowest ranges. There are several indications that the actual N_2O-emission in real-life might be lower than the values indicated in this report, leading to an asymmetric uncertainty margin, roughly estimated at plus 25% and minus 50%.

Contents

1 Introduction

In a realistic determination of the contribution of traffic to the total greenhouse effect, the emissions of N_2O need to be included into the consideration. Within the framework of the ROB-programme of the Dutch authorities (ROB = Reductie Overige Broeikasgassen: reduction of other greenhouse gases) attention is paid to this aspect. N_2O is high on the list of gases that require attention, since the effect of N_2O relative to CO_2 amounts to a factor of 296. That means that a relatively small amount of N_2O-emission can translate into a significant CO_2-equivalent.

In the past, estimates have been made of the amount of N_2O emitted by Heavy Duty (HD) vehicles. These were based on an assumed relation between the NO_x-emission and the N_2O-emission. Based on this assumption, a rather high N_2O-emission has been estimated for HD vehicles (30 mg/km according to the IPCC). This assumption has never been substantiated, however, by a large scale-measuring programme. For passenger cars such an inventory has taken place relatively recently [1]. This showed that especially for passenger car diesel engines without an exhaust gas after-treatment system the N_2O problem is relatively minor.

The emission of N_2O does occur especially with the use of platinum (or other active metal) based catalysts for the after-treatment in combination with specific exhaust gas conditions. This fact, together with the results from the N_2O inventory for diesel engined passenger cars, led to the expectation that the present and earlier HD engines without catalyst emit hardly any N_2O. But no hard conclusions could be drawn as no actual measurements could validate this assumption. For future engines with advanced exhaust gas after-treatment systems on the other hand the expectation was that they could indeed emit N_2O. A measurement in the project mentioned, on a Euro 3 HD diesel engine equipped with a catalytic particulate trap showed that for this kind of technology the N_2O-emission is indeed present, although not very high (11 mg/km or 0.5 % equivalent CO_2-emission).

In order to assess the N_2O-emissions of HD vehicles, a research project was set up with a measurement programme. The main objective of this project is to determine the contribution of Heavy Duty vehicles to the national emissions of greenhouse gases in the Netherlands -N_2O-emissions in particular- for engine technology applied within the period from 1995 until now. The results of the measurements should allow for an extrapolation of the N_2O-emission factor prediction from the year 1988 up to 2010. For the purpose of cost reductions, a synergy with measurements for other research projects was pursued. So as to obtain in any case a good impression of the N_2O-emissions for the current HD vehicle fleet (Euro 3 engine technology) a connection has been made with the In-Use Compliance Programme for Trucks 2001-2003, that TNO carries out on behalf of the Ministry of the Environment (VROM). Some projects at TNO comprising a demonstrator vehicle with prototypes of catalyst after-treatment technology provided insight in N_2O-emissions of future engine technology.

This report gives a description of the activities that have been carried out in order to map out the N_2O-emissions from trucks, and gives the results and analyses that followed from this measurement programme. The most relevant information and results are described in the main report, while in-depth backgrounds and specific measurement details are given in appendices.

2 N_2O formation in catalytic after-treatment technology of diesel engines

2.1 Introduction

This chapter is based on the findings of Feijen et al. [2], who reviewed the theoretical background of N_2O-emissions from three-way catalysts and up-coming technologies for diesel after-treatment. The Feijen-review was updated through a search in literature databases and on Internet; an overview of the literature search results can be found in Appendix A. The information coming from this review is incorporated in this chapter.

The exhaust gas of a diesel engine contains some hydrocarbons and CO but mainly NO_x and particulate matter. Just as observed for gasoline engines, the N_2O-formation in the combustion chamber is generally rather low. However, N_2O might be emitted when the exhaust gas is treated. The combination of a relative low exhaust gas temperature and the specific active metals used in e.g. particulate filtration or the catalytic reduction of NO_x might cause N_2O-formation similarly to N_2O-formation during start-up over three-way catalysts in gasoline cars. For a detailed description of these processes refer to Appendix B.
At present (2003), diesel exhaust after-treatment systems are not common practice for HD diesels. In the coming decade after-treatment will be introduced on a large scale to meet future emission legislation, especially for truck diesel engines. Therefore increased N_2O-emissions might be expected in future.

This chapter first describes the developments of the emission legislation and the after-treatment technologies which are applied (or expected to be applied) to control the exhaust gas emission of diesel engines. In addition, the possibility of N_2O-emission is discussed.

2.2 Heavy Duty diesel after-treatment systems

Development of legislation
The Heavy Duty category consists of engines for vehicles with a total maximum weight of above 3500 kg. For legislation, the Heavy Duty diesel engines are tested on an engine dynamometer. The current and future European emissions legislation for truck diesel engines is presented in Table 2.1. It must be noticed that the testcycle depends on the legislation and the engine technology. Three different cycles are used:

- ECE R49: 13-mode steady-state testcycle used up to Euro 2.
- ESC: European Steady-state Cycle: 13-mode testcycle with new mode points and weight factors compared to ECE R49. This better represents average European driving conditions.
- ETC: European Transient Cycle. This cycle needs to be carried out in addition to the ESC if the engine is equipped with advanced exhaust after-treatment such as a particulate trap or SCR-deNO_x.

Year		Euro 2 1996	Euro 3 2000		Euro 4 2005		Euro 5* 2008	
Cycle		ECE R49	ESC	ETC	ESC	ETC	ESC	ETC
NO_x	g/kWh	7	5		3.5		2	
PM	g/kWh	0.15	0.1	0.16	0.02	0.03	0.02	0.03
CO	g/kWh	4	2.1	5.45	1.5	4	1.5	4
HC	g/kWh	1.1	0.66	0.78	0.46	0.55	0.46	0.55

* Limit values and testcycle still uncertain; CNG-engines also have additional CH_4-emission limits

Table 2.1 - European emissions legislation for truck diesel engines.

All testcycles are run on an engine dynamometer, so only the engine is tested. Emissions are expressed in gram per kWh. The testcycles have a "warm" start; this means that engine is already warmed up and running at the start of the test. Cold start emissions do no play a large role in the overall emissions, since trucks are usually used during a large proportion of the day.

Development of state-of-the-art HD diesel technology

The more strict legislation causes improvements in state-of-the-art technology. Table 2.2 gives an overview of measures for emission reduction that are applied and the measures that most likely will be applied in future. The exhaust after-treatment systems will be dealt with briefly in this paragraph. More details on the operating principles and the N_2O formation can be found in Appendix B.

Euro class	year	Measures for emission reduction
Euro 2	1996	2 or 4 valves per cylinder some engines have fuel injection with timing control
Euro 3	2000	4 valves per cylinder Advanced injection systems (unit pumps, unit injectors or common rail, all with electronic timing control) Advanced turbo-charging Cooled EGR (only applied by one manufacturer at this time).
Euro 4	2005	Advanced injection systems Advanced turbo-charging Oxidation catalyst, SCR $DeNO_x$ and NH_3-clean-up. (alternative for smaller engines: Cooled EGR plus a CRT particulate filter)
Euro 5	2008	Advanced injection systems Advanced turbo charging Oxidation catalyst SCR $DeNO_x$ and NH_3-clean-up in combination with a NO_x-sensor (alternative for specific applications: CRT particulate filter)

Table 2.2 - Development of state of the art diesel technology
Exhaust gas control until Euro 4

At present diesel engine emissions are controlled through various in-engine measures. Newest developments are:

- High pressure injection system with timing control and rate shaping (both to reduce NO_x and particulates emissions), that allow for a very accurate dosing of the diesel, and adapted to the engine load condition.
- Advanced turbo-charging systems (e.g. variable turbo geometry) to allow for a more flexible combustion air supply, high power output and high air/fuel ratio.
- Exhaust Gas Recirculation, which redirects a part of the exhaust gas back to the inlet manifold through a controlled valve. This affects the combustion chamber temperature and the air/fuel ratio, with the objective to reduce NO_x-emissions.

All HD engines are nowadays of the direct-injection type (DI). This engine principle is primarily applied to increase engine efficiency and thus to reduce the fuel consumption, but it increases engine out NO_x-emissions at the same time. In combination with the shift to direct injection, more advanced electronically controlled injection systems have been applied. These systems (unit injector, common rail) can be closely linked to the specific demands of the newest exhaust gas after-treatment systems. For instance, post injection of fuel in order to increase exhaust gas temperatures during regeneration of soot filters.

Exhaust gas control from Euro 4 and beyond
The emission limits for Euro 4 and beyond are so strict that engine measures (design and combustion process modifications) are no longer satisfactory to meet these limits. As a result, exhaust gases will have to be after-treated. Most likely a combination of exhaust gas after-treatment systems will be applied: separate stages have to be used to reduce the (1) particulate emissions (which might comprise the oxidation of NO into NO_2) (2) HC and CO-emissions, (3) NO_x-emissions, and (4) a slip of NH_3 from NO_x-reduction. The following technologies are being applied or expected to be applied to comply with the Euro 4 and 5 emission limits:

With respect to particulate emission reduction, post-2005 technology is not clear yet. Most likely particulate emissions limits can be met through in-engine measures at the cost of increased engine-out NO_x-concentrations. These increased NO_x-concentrations do not create problems, since efficient deNO_x-measures will be taken. For special applications particulate filters will be applied. Two types of soot-filter are promising:
Continuously Regenerating Trap (CRT) of Johnson Matthey: This uses a very active oxidation catalyst (platinum) upstream of the filter. The oxidation catalyst converts NO in NO_2, which consequently acts as a reagent to react with the collected soot in the filter. The soot is then converted in CO_2 and removed from the filter.
Catalysed Soot Filter (CSF) of Engelhard: A platinum coating is applied to the soot filter itself. This secures regeneration in two ways: platinum catalyses the direct soot oxidation with O_2, but also induces the oxidation of NO into NO_2, which is a much better oxidant for soot than either NO or O_2.

HC and CO-emissions will be mitigated through an oxidation catalyst. The oxidation catalyst enables the reaction at exhaust temperatures of HC and CO with O_2 to produce CO_2 and H_2O. Oxidation catalyst technology is well established and there are several suppliers. Most oxidation catalysts are based on platinum as the active component.

In Europe, *NO_x-emissions* will most likely be reduced by selective catalyst reduction (SCR) with urea. In the exhaust gas, urea is decomposed to NH_3 and CO_2, and the NH_3 reacts catalytically with NO_x to form N_2 and H_2O. SCRdeNO_x is proven technology for stationary installations and is very efficient in NO_x-emission reduction with efficiencies

above 90%. At the moment several consortia are in the process to demonstrate SCR-technology for automotive Heavy Duty diesels and results seem promising. So this technology will most likely become the standard in Europe, despite investments required for the urea-distribution infrastructure. In the USA, NO_x-storage catalysts are considered to be the most promising.

The dynamic character of NO_x-emissions complicates urea injection in the SCRdeNO$_x$; too little urea increases NO_x-emissions, too much urea might lead to *NH_3-slip*. To enable sufficient urea dosage and simultaneously avoid NH_3-emissions, a NH_3-clean-up catalyst will most likely be used. This is an oxidation catalyst, with Pt, Ag or Cu as an active phase that converts NH_3 with O_2 into N_2 and H_2O.

2.3 Impact on N_2O-emissions

Table 2.3 speculates on possible N_2O-formation in diesel exhaust after-treatment. This speculation is based on the more fundamental knowledge of the relevant processes described in Appendix B, and the scarce literature on this topic (see Appendix A). All catalytic after-treatment systems, that contain noble metals such as platinum, rhodium and palladium, may produce N_2O by the reaction of NO_x with hydrocarbons under lean reaction conditions. For rhodium (in three-way catalysts), this non-selective reduction of NO is known to occur at temperatures around 200 °C to 250 °C (see figure 2.1). For platinum and palladium, the peak in N_2O-emissions will most likely be in the same temperature window.

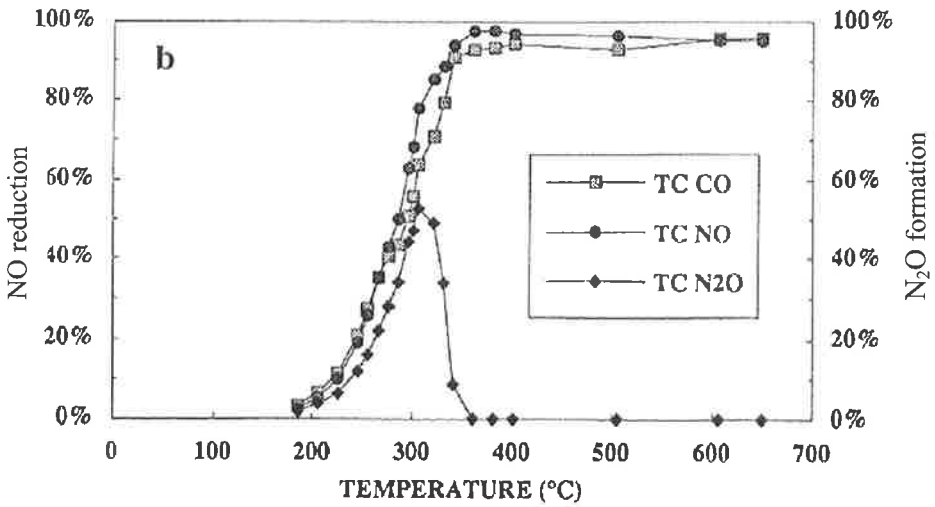


Figure 2.1 - NO reduction with CO over a three-way catalyst (TC, 1%Pt-0.2%Rh/Al_2O_3); conversion of NO and CO and the formation of N_2O vs temperature [3]

System	Possibility N_2O-formation
No catalytic after-treatment	Negligible N_2O-emissions
Catalysed soot filter	Contains Pt, in principle able to produce N_2O
Continuous regenerating trap	Contains Pt, in principle able to produce N_2O
Oxidation catalyst	Contains Pt, in principle able to produce N_2O
Urea-SCR-DeNO_x	No indications for N_2O-formation when applied under proper conditions,
NH_3-clean-up catalyst	N_2O can be formed by oxidation of excess NH_3 at high temperature over the oxidation catalysts that makes up the last element in NH_3-SCR

Table 2.3 - Possibility of N_2O-emission from diesel after-treatment

Diesel engines without after-treatment in general have negligible N_2O-emissions.
Oxidation catalysts and catalysed soot filters on diesel engines will most likely cause some N_2O-emissions, though earlier measurements indicate that emissions are low compared to N_2O-emissions from gasoline-fuelled cars with three-way catalysts [2]. Developments in increased engine-efficiency (and thus reduced exhaust temperature) might affect N_2O-emissions further. Earlier dynamometer-measurements at TNO support this expectation. An increased emission (8 mg km^{-1}) is observed from Euro 3 diesel passenger cars, compared to Euro 1 (without oxidation catalyst, 2 mg km^{-1}) and Euro 2 cars (5 mg km^{-1}) [2]. This observation however, is based on a small amount of measurements. The observed N_2O-emission is small compared to emissions from three-way catalysts.
There has been a lot of attention towards SCRdeNO_x and on the basis of findings in literature N_2O-emission is not expected from urea-SCR systems, provided that proper reaction conditions are applied. However there are indications that when an additional platinum catalyst is used for the oxidation of NH_3 in the slipstream of the SCR-unit, N_2O can be formed.

3 Measurement programme

3.1 Selection of vehicles

The preceding chapter clearly indicates that the HD engine technology (more specific the type of after-treatment device) influences the level of N_2O-emissions. In order to cover the full range of engine technology applied over the period from 1988 until 2010, a measurement programme consisting of the following vehicle types was set up:

- *Euro 1 vehicles*
  Though there is no fundamental reason to assume that N_2O-emission levels of Euro 1 vehicles would differ much from Euro 2 or 3 vehicles, no actual measurements have been performed before to verify this. As the results would have to allow for an extrapolation to 1988 emission levels, it was found necessary to examine differences in N_2O-emissions between Euro 1 and 2, if any. A sample of 3 vehicles was thought to be the minimum requirement for a representative emission factor of this vehicle class.
- *Euro 3 vehicles*
  TNO performs the 'In-Use Compliance programme for trucks' for the Dutch Ministry of Housing, Spatial planning and Environment. This project involves the testing of a representative share of the HD vehicle fleet in the Netherlands, to check the in-use emissions in comparison with their respective type approval emission values. During the time that the N_2O measurement programme was running, 29 vehicles were tested for the IUC programme. This provided the opportunity to screen the N_2O-emissions at the same time.
- *Demonstrator vehicles*
  For the purpose of estimating future emission levels of N_2O from HD vehicles, three prototype vehicles were tested; two with an experimental urea SCRdeNOx system and one with EGR and a diesel particulate filter. For the vehicles with urea SCRdeNOx the NH_3-emissions were screened as well. At this moment, the general consensus within the HD vehicle industry is that the SCRdeNOx system will be applied to fulfil both Euro 4 and 5 emission limits, without the need for additional after-treatment systems.
- *Urban buses with CRT filters*
  The Continuous Regenerating Trap (CRT) is a type of after-treatment system that is frequently used as a retrofit application to reduce particulate emissions from urban buses. Upstream of the filter, a platinum based pre-oxidation catalyst is installed to convert NO into NO_2. This catalyst may also produce N_2O as a by-product. Five Euro 2 buses equipped with a CRT filter were screened on N_2O-emissions. Sampling was done both upstream and downstream of the CRT, so the engine-out N_2O-emission level could also be determined as extra information to fill the 'gap' between Euro 1 and Euro 3 vehicles.
- *CNG vehicles*
  During the course of the project, it was decided that including CNG technology into the measurement programme would provide a more complete overview, especially since CNG engines are usually fitted with after-treatment systems. There are basically two different CNG technologies used:
  – Stoichiometric engine with a lambda controlled three-way catalyst
  – Lean-burn engine with an oxidation catalyst (uncontrolled)
  For both categories a representative vehicle was chosen. N_2O-emissions may be expected from three-way catalysts, just as is observed for petrol passenger cars. On a

lower scale, the oxidation catalyst for the lean-burn engine is also capable to produce some N_2O (see also Paragraph 2.3). For the future it is expected that the lean-burn technology is the most promising.

- *Engine tests*
  The project budget allowed for a prototype engine with after-treatment technology to be screened for N_2O-emissions on the transient engine testbed, if an opportunity occurred to combine this with already planned measurements for such an engine. It was considered very valuable to the project if transient N_2O results could be added, to provide insight in real-life N_2O-emission behaviour. Unfortunately there were no possibilities to do these measurements during the course of the project; some engines with experimental after-treatment systems have been tested on the engine testbed in other projects, but there was no opportunity to include measurements of N_2O-emissions in these tests.

3.2 Testing activities

The testing activities for N_2O screening are described in detail in Appendix C. Basically, the test comprises a simulated ESC 13-mode test on a steady-state chassis dynamometer. For the Euro 1 and 2 vehicles the conventional ECE R49 13-mode test is used, while for Euro 3 the ESC test was performed. During the 13 modes, the N_2O-concentrations are measured continuously, including the transitions from one mode to the next. The latter provides a global impression of the effect of transient engine behaviour on the N_2O-emissions, though the ESC test is principally a steady-state test. Apart from N_2O, also the regulated emission components are measured (CO, HC, NO_x, and PM) in order to assess the general (maintenance) condition of the engine, and to search for a possible correlation between NO_x and N_2O.

3.3 Test experiences

Most of the measurements were successful, and generally have been executed without any difficulties. The only problems encountered concerned the CRT filters on the buses (see Paragraph 4.1). For further details about the test experiences refer to Appendix D.

4 Results

4.1 Measurement results

In this paragraph the results are described in general for each of the vehicle classes within the measurement programme. More detailed results and information on the individual vehicles can be found in Appendix D.

Euro 1 vehicles
Within this category three vehicles have been tested. Apart from N_2O-emissions also the regulated emission components were measured, in order to get an impression of the engine condition. None of the vehicles emitted well measurable N_2O-levels; the absolute measurement signal (2 ppm at maximum) was hardly above the minimum detection level of the analyser. It is not even sure whether this low signal is induced by an actually present N_2O-concentration; this kind of analyser also shows some cross-sensitivity for CO_2-emissions.
The engines have also been tested with a cold engine. The measured N_2O was at about the same low level as in the 'hot' test.

Euro 3 vehicles
During the time that this measurement programme was running, 29 vehicles were tested for the Dutch IUC programme. These vehicles have all been screened on N_2O-emissions. Most engines proved to be in good condition because they were in accordance with the manufacturer specifications, and fulfilled the applicable type approval limits. Only one engine type (three vehicles with this engine were tested) encountered some problems to comply with the Euro 3 emission standards. This problem was resolved, and will most likely not have affected the N_2O-emission. One engine type (two vehicles tested) was equipped with an EGR system; all other vehicles did not have any kind of exhaust after-treatment device installed.
The N_2O-levels of all Euro 3 vehicles were hardly measurable, therefore the same note for the analyser applies (see Euro 1 vehicles).
For a number of Euro 3 vehicles the N_2O-emissions were also screened during a 'cold' 13-mode test. This did not seem to affect the absolute N_2O-level.

Euro 2 buses with CRT filter
All five vehicles that were planned in the measurement programme have been tested. Emissions of N_2O were quite low, on average 1 to 2 ppm, with occasional peaks of 4 to 12 ppm. When the official ESC weighting factors are applied (taking the average N_2O-emission level over the last 30 seconds of the modepoints), the overall N_2O-emission result ranges from 0.01 to 0.02 g/kWh. The buses have also been tested with a cold engine. This seemed not to affect the levels of measured N_2O. Upstream of the CRT filter the N_2O level was hardly above the minimum detection level.
Some problems were encountered with the CRT filters. During normal daily operation the exhaust temperatures of the buses remain at a relatively low level. Exhaust temperatures during the ECE R49 13-mode test reach considerably higher levels than in normal operation. As a result, the stored soot on the filter will oxidise rather instantaneously (uncontrolled exothermal reaction). The accompanying high temperatures may cause damage to the filter. This problem revealed itself during the tests on the first two buses. After consulting the manufacturer it was decided to oxidise the soot on the filter in a controlled way, by putting the filter into an oven prior to the test. Afterwards the filter was remounted, and a 'preparation test' was performed in which the exhaust

gas temperature was brought to about 300°C for half an hour. These preparations proved sufficient to test the remaining three vehicles without any further problems.

It is most unlikely that the results on the first two buses have been affected by this problem. The N_2O-emissions are mainly formed in the oxidation catalyst upstream of the filter, which functioned normally during the tests.

Demonstrator vehicles
In total three prototype vehicles were tested; two with an experimental urea SCRdeNOx system and one with EGR and a diesel particulate filter. For the vehicles with urea SCRdeNOx the NH_3-emissions were screened as well. All vehicles were in good condition and complied with the specifications of the manufacturer.
The vehicles with SCRdeNOx systems produced the highest N_2O-emission levels within the measurement programme, though the absolute levels are still quite low. This was contradictory to the expectations, especially since both vehicles did not have a NH_3 clean-up catalyst in the after-treatment system. Over the testcycle, an average emission level of 2.5 to 7.5 ppm was measured and occasional peaks to 30 ppm at maximum. When the official ESC weighting factors are applied (taking the average N_2O-emission level over the last 30 seconds of the modepoints), the overall N_2O-emission result ranges from 0.03 to 0.07 g/kWh. To put this value in perspective: the Euro 3 limit for NO_x-emissions is 5 g/kWh. The average NH_3-emission for the SCRdeNOx systems ranges from 6 to 11 ppm on average. Although this is somewhat higher than the N_2O-emissions measured, it can still be regarded as rather low.
The vehicle with EGR and a diesel particulate filter did not produce well measurable N_2O-emission levels, either in the 'warm' or 'cold' test.

CNG vehicles
The first vehicle tested was a Volvo refuse collection vehicle, with a lean-burn Euro 2 engine and an oxidation catalyst. The engine appeared to be in good condition, though the NO_x-emission was at a rather high level. By consulting the maintenance shop it was found out that an alternative EPROM was used in the engine control system. This enables a somewhat richer mixture, resulting in higher engine power and torque and -as a consequence- more NO_x-emission. Despite the higher NO_x, the N_2O-emission was hardly measurable: 0.6 ppm on average, and a highest peak of 7.5 ppm. When the official ESC weighting factors are applied (taking the average N_2O-emission level over the last 30 seconds of the modepoints), the overall N_2O-emission result is well under 0.01 g/kWh.

The other vehicle was a Euro 2 MAN refuse collection vehicle, with a stoichiometric lambda-controlled engine and three-way catalyst. Over the 13-mode test the control system did not seem to be able to keep the lambda at '1'. In a stoichiometric engine with a three-way catalyst, even small deviations from the lambda = 1 setting (so-called 'lambda excursions') immediately result in higher NO_x-emissions (lambda > 1) or higher CO and HC-emissions (lambda < 1). In this case, the leaner mixture clearly caused high NO_x-emissions, and consequently also N_2O-emissions. On average this amounted to 5 ppm, with a highest peak of 23 ppm. When the official ECE R49 weighting factors are applied (taking the average N_2O-emission level over the last 30 seconds of the modepoints), the overall N_2O-emission result is 0.06 g/kWh.
Because of the high NO_x-emission, the measured N_2O-emission could not be considered to be representative for this kind of CNG technology. The manufacturer of the vehicle was consulted in order to find the reason for the unusual emission behaviour. After a thorough inspection and adjustments made to the fuel system, it was found out that the EPROM used in the ECU is not suitable for the CNG quality used in

the Netherlands. A second test was performed, after the correct EPROM was installed. The NO_x-emission now decreased to a comparable level of the type approval value, and as a consequence also the N_2O-emission dropped to 0.02 g/kWh over the ECE R49 test (on average 3 ppm, with a highest peak of 8 ppm). There are strong indications that the N_2O-emission is even lower than 0.02 g/kWh (see Appendix D), so this value can be seen as a maximum.

After the first test, the vehicle was also tested with a cold start (not a full 13-mode test). Both NO_x- and N_2O-emissions were at a considerable lower level than in the hot test. Apparently, during the cold test the engine remained a shorter period in the temperature window favourable for N_2O formation.

General impact on greenhouse-effect
The Global Warming Potential factor for N_2O (relative to the GWP of CO_2) is 296 according to the IPCC (Intergovernmental Panel on Climate Change) [11]. With this factor, the equivalent CO_2-emissions can be calculated for the different engine technologies tested in this programme:

- Euro 1, 2 and 3 vehicles with conventional engine technology: < 3 g/kWh
- Euro 2 buses with CRT filter: 3 to 6 g/kWh
- Demonstrator vehicles with SCRdeNOx after-treatment systems: 9 to 21 g/kWh
- Euro 2 vehicles with CNG technology: <3 g/kWh (lean-burn) or <6 g/kWh (stoichiometric)

The CO_2-emission range for current HD engines over a 13-mode test is 630 to 720 g/kWh. This means that the maximum contribution of N_2O to the greenhouse effect for future HD vehicles equipped with SCRdeNOx after-treatment (in percentage of the CO_2 contribution) is not more than 3.5%. For the other engine technologies tested this percentage is even considerably lower (in the range of 0 to 1%).

4.2 Analysis of the results

Correlation of NO_x- and N_2O-emissions
As was already mentioned in the introduction, estimates for N_2O-emissions of HD vehicles have in the past been based on an assumed relation between the NO_x- and the N_2O-emission. This assumption was derived from some measurements done on passenger car vehicles. In general, the NO_x-emission of diesel trucks is relatively higher than that of passenger car diesel engines, so if this assumption proves wrong, it may very well lead to an overestimation of the N_2O-emissions. This correlation will be further assessed here. For a comparison between the N_2O-emission factors found in this project relative to the 'common' factor used by the IPCC, please refer to Chapter 5.

First of all it can be concluded that the assumption made can only be valid for engines with after-treatment systems, since the N_2O-emission from Euro 1 until Euro 3 is at the level of almost zero. For Euro 1 vehicles a maximum NO_x-emission of 9 g/kWh over the ECE R49 was allowed in Directive 91/542/EEC, which is almost double the Euro 3 limit of 5 g/kWh over the ESC test (Normally, the NO_x-emissions of production engines are close to the legislative NO_x-limit). Nevertheless, the N_2O-emission measured for both engine technologies is of the same order of magnitude. So a direct relationship between NO_x and N_2O does not seem present for conventional engine technologies.

Figure 4.1 shows the N_2O-emission versus the NO_x-emission of the second vehicle with SCRdeNOx system. There is no straightforward correlation between these emissions

visible. The only conclusion from this figure may be that the availability of NO_x is a prerequisite for N_2O-emissions, or in other words: the actual NO_x-emission determines the upper limit of N_2O-formation. This is rather obvious, since N_2O is formed from adsorbed N and NO.

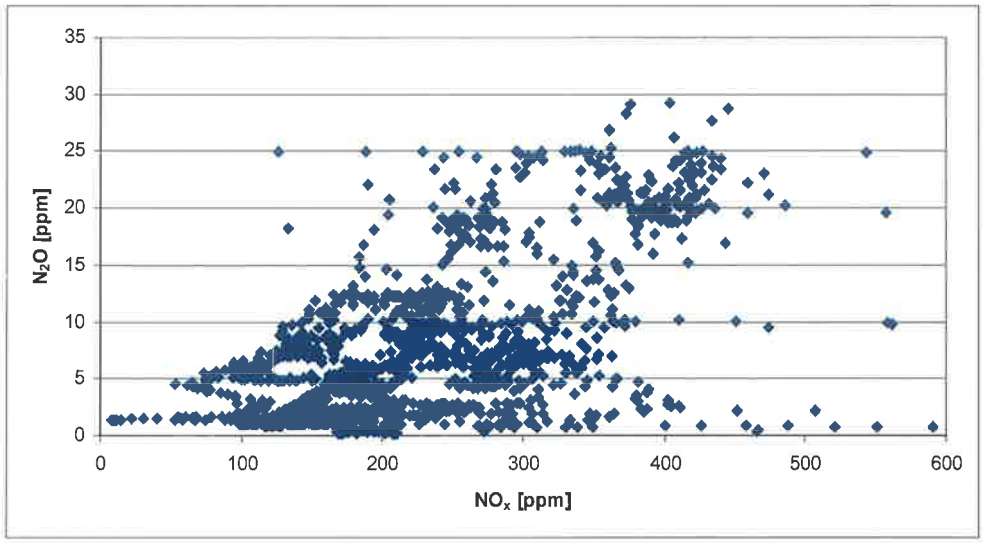


Figure 4.1 – Online N_2O-emissions as a function of NO_x-emissions for the second SCRdeNOx vehicle.

More or less the same is observed for the other engine with SCRdeNOx system.

The results for buses with CRT filter are somewhat different, but also here no obvious correlation is found (see Figure 4.2). More or less the same conclusion as made for Figure 4.1 applies.

The peak at ca. 650 ppm NO_x is the result of a short N_2O peak, during which the NO_x-emission remained almost at a constant level.

From these results it is safe to say that the assumed correlation between N_2O- and NO_x-emissions was wrong. The truth is better reflected by the following statement:
Higher NO_x-emission *may lead* to higher N_2O-emission, but a higher N_2O-emission is *not the result of* an increase in NO_x-emission. Various other aspects play at least an equally important role, such as exhaust gas temperature and catalyst composition.

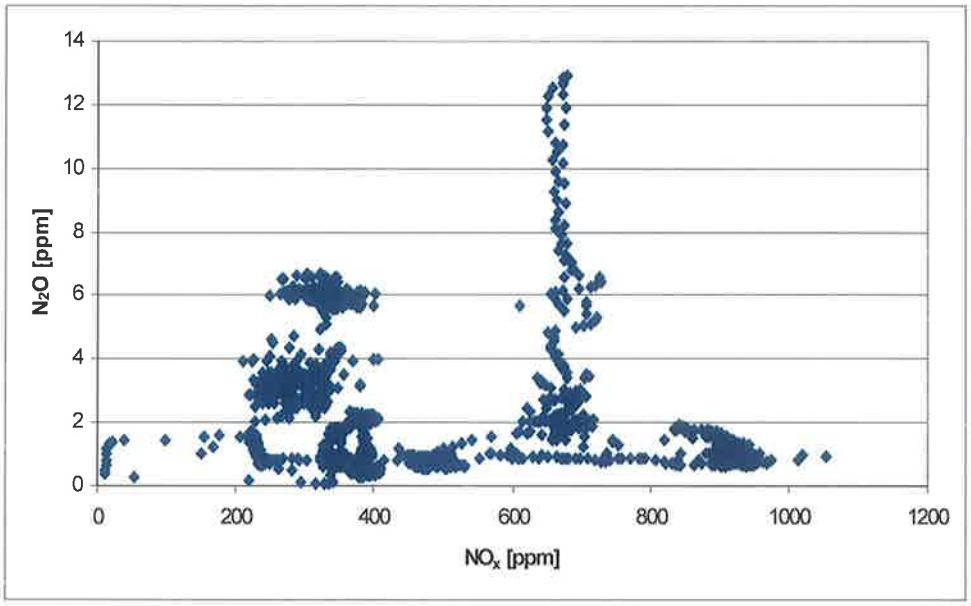


Figure 4.2 - Online N_2O-emissions as a function of NO_x-emissions for the third bus with CRT filter

Test inaccuracies

In Paragraph 4.1 some reservations were already made towards the actual N_2O-emission when the analyser signal is rather low. The accuracy of an analyser is obviously limited. For an overview of the analyser details and specifications, please refer to the end of Appendix C. A number of factors will affect the accuracy of the measurement, such as drift, noise and non-linearity. The lower detectable limit of the analyser is 0.3 ppm, and cross-sensitivity for CO_2 introduces an extra inaccuracy of about 1 ppm for usual CO_2-concentrations in these tests (the CO_2 is measured as N_2O by the analyser, so the real N_2O-emission is *lower* than indicated by the measurement signal). Finally, there is also some background N_2O-emission of 0.3 ppm in the atmosphere. For the results it is assumed that the actual N_2O-emission can not be determined when the measurement signal is in the range of 0-2 ppm. In those cases the N_2O-emissions are presented as a 'lower than …' value. For higher N_2O-concentrations an inaccuracy of –1 to 2 ppm is taken into account.

Another cause for an inaccurate result is the N_2O-formation process itself. Normally, emissions will stabilise over the time that a mode is tested (2 or 6 minutes for the ESC or ECE R49 13-mode test respectively). The emission level over the last 30 seconds is averaged (60 seconds for ECE R49 test), and is seen as the representative value for that mode. In case of N_2O, the emission level is rising constantly over the mode, and has sometimes not reached an equilibrium before the end of the mode. See as an example Figure D.8 in Appendix D for the first SCRdeNOx vehicle. The reason for this behaviour can be found in the close relation between N_2O-formation and exhaust gas temperatures. In the lower temperature range the N_2O is formed, but not released until higher temperatures are reached. A detailed explanation for this behaviour is given in the section *N_2O-emission behaviour*. Taking the average emission level over the last 30 or 60 seconds can obviously not be seen as a 'representative' emission for that mode. In order to come to a good understanding of the 'real' N_2O-emission, also the exhaust gas temperature has to be observed.

The 13-mode test is a static test, during which the temperatures and pressures in each mode are allowed to stabilise. In real-life situations, the engine is operated more

dynamically, and especially temperatures will not stabilise due to the thermal inertia within the engine. Therefore it is safe to assume that the higher exhaust gas temperatures recorded during a 13-mode test (under which higher levels of N_2O are emitted) will not be seen easily in normal operation, simply because the engine will not be given sufficient time to reach these levels. This remark particularly concerns the high load points (75 and 100% load), that are only used shortly in acceleration phases, not for longer periods with constant engine load. These were also the modes where the highest N_2O concentrations were measured. As a conclusion, the emission levels for N_2O in this report can not be seen as a correct absolute level, however they provide a good indication of the upper limit of N_2O-emissions.

N_2O-emission behaviour of CRT filters

The N_2O-emissions from CRT-filters are in general very low; N_2O-peaks in the exhaust are limited to 4 to 12 ppm. For comparison: in three-way catalysts, N_2O-peaks up to 200 ppm are observed. A closer evaluation of the results shows that increased emissions occur at relative cold exhaust gas temperatures. In Figure 4.3 the N_2O-emissions and pre-catalyst exhaust gas temperature are plotted in time. N_2O-emissions are only observed in the period until 1450 seconds when the exhaust gas temperatures is 200 °C at maximum, and again at about 2900 seconds after cooling down during a 5 minutes period when running idle a small peak in emissions is observed.

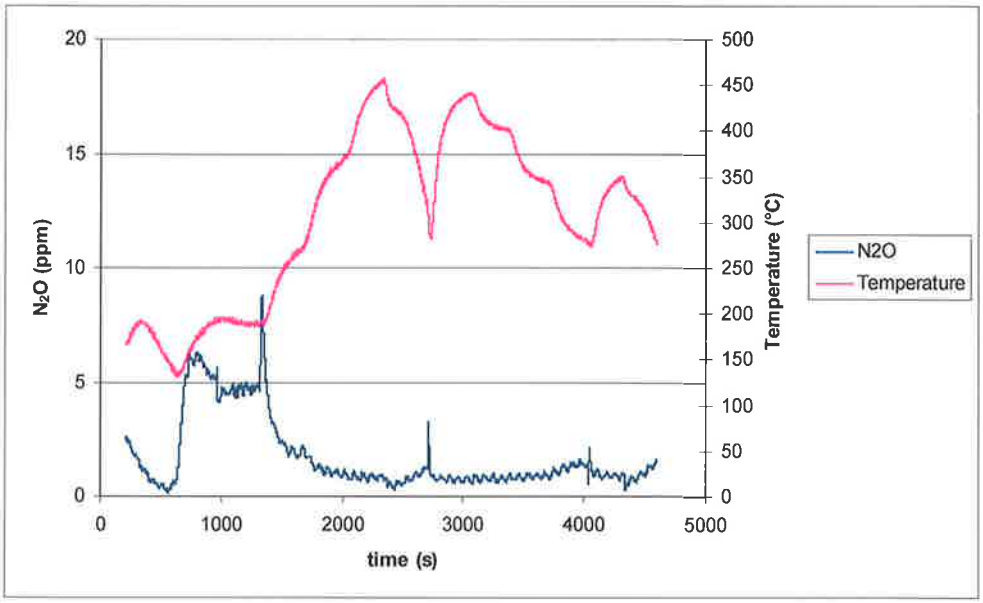


Figure 4.3 - N_2O-emissions and exhaust gas temperature (upstream catalyst) over a CRT filter

When N_2O-concentrations and exhaust gas temperatures (upstream catalyst) are plotted against each other, the maximum N_2O-emissions are observed at temperatures between 150 and 230 °C (see Figure 4.4). The existence of such a temperature window is in line with literature (see Paragraph 2.3 and Appendix B). However the temperatures at which the N_2O-emissions peak are lower than expected. The hook-shaped curve at the bottom-left of the graph is recorded during the idling part of the test. The relatively low exhaust flow stream is the most probable cause for the inconsistent behaviour of that part.
This relatively low N_2O-formation temperature window is observed for all the buses with a CRT filter.

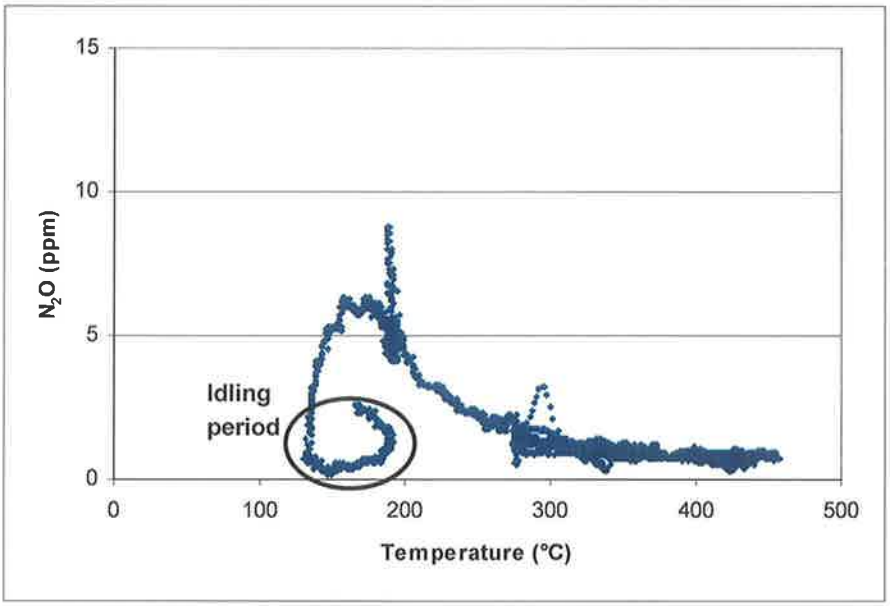


Figure 4.4 - N_2O-emissions versus exhaust gas temperature (upstream catalyst) over a CRT filter

The very low N_2O-emissions of the demonstrator vehicle with EGR and a CRT are in contrast with the findings on the buses with CRT filters. This can be attributed to two aspects:

- the relative low engine out NO_x-concentrations (on average 330 ppm for the EGR demonstrator versus 525 ppm for HD vehicles with only CRT). As indicated just before, lower NO_x-concentrations will limit the N_2O-emission peaks.
- The EGR system has a dampening effect on the exhaust gas temperatures; at lower engine loads it is higher and at higher engine loads it is lower. Most of the time the engine is not operated in the temperature window at which maximum N_2O-emissions occur for CRT filters (between 150 and 230 °C). Still, some minor N_2O peaks would have been expected for the short time that temperatures were below 230 °C. These peaks did not occur in the test.

N_2O-emission behaviour of SCRdeNOx systems

According to literature, N_2O-emissions from SCRdeNO$_x$ systems will probably be limited. The most likely source for N_2O-formation is an unselective oxidation of excess NH_3 over the clean-up catalyst at low temperatures (see Paragraph 2.3 and Appendix B). However, the dynamometer tests were done with SCRdeNO$_x$ systems without NH_3 clean-up catalysts. Therefore, the emission of N_2O is unexpected and also the temperature at which it takes place is at an unexpected high level: roundabout 400 °C.

The origin of this N_2O-emission is unclear. A few remarks can be made however, that might explain the discrepancy between the current results and literature:

- Stationary systems for NO_x-reduction (as applied in industrial processes) are not operated as dynamic as automotive SCR and they might be more selective towards NO_x-reduction into N_2 and O_2 (amongst others also resulting in less ammonia slip)
- Absolute levels of N_2O are relatively low compared to N_2O-emissions in three-way catalysts. The peak of 20 ppm is about 10 times less than the peak-concentrations that can be found in three-way catalysts. It is possible that such a low generation of

N_2O is considered negligible in many NO_x lab-scale and full-scale SCR-deNO_x-experiments, and is therefore not reported.

The high temperature of emissions is most likely caused by N_2O-desorption. A closer observation of results shows that N_2O-emissions are at their highest when the temperature is increasing. This becomes very clear when the N_2O-emissions are plotted against the temperature for the first 500 seconds of the test (see Figure 4.5). Within this period, the highest peak of N_2O occurs (refer to Figure D.8 in Appendix D). This N_2O-peak shows a hysteresis: a slow increase in emissions as long as the temperatures is rising, followed by a sharp decrease in emissions when the temperature drops (the other peaks in the same test have the same pattern, although not that pronounced, since average emissions are somewhat smaller).

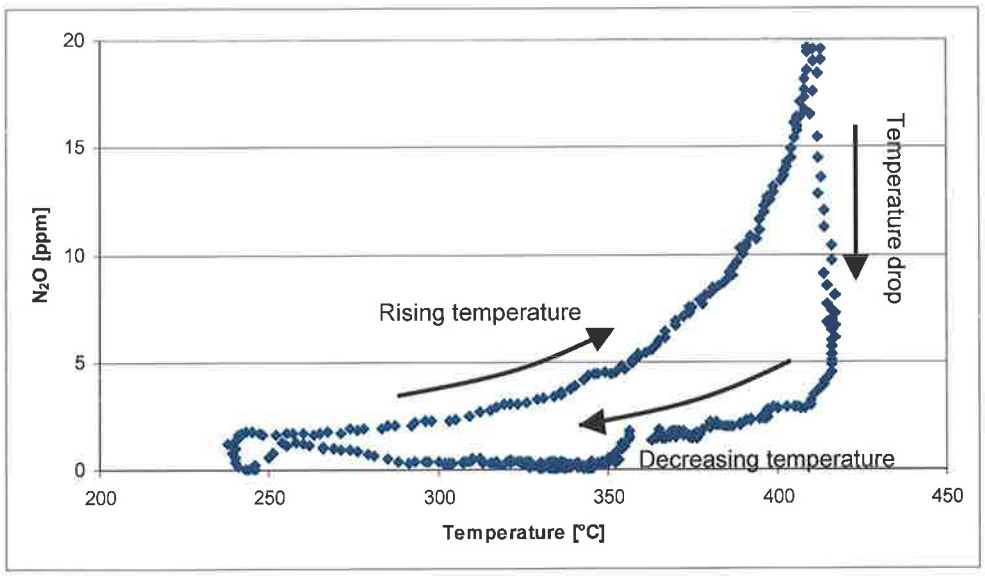


Figure 4.5 - N_2O-emission versus exhaust gas temperature for a SCR-deNO_x-catalyst for the first 1000 seconds of the test

The hysteresis loop is characteristic for experiments where N_2O-desorption determines the N_2O-release. At the start of the temperature increase, the catalyst surface is most likely covered with adsorbed N_2O, possibly produced from adsorbed NO and N at lower temperatures (see mechanism in Appendix B). With temperatures rising N_2O is increasingly desorbed, leading to increased N_2O-concentrations in the exhaust gas. When the temperature rise ceases and the cooling down sets in, there is no driving force anymore for N_2O-desorption and concentrations in the exhaust gas drop almost instantly.
However, this does not explain why subsequent increases in temperature again result in N_2O-emissions. When the catalyst has reached 400 °C and has lost its N_2O until adsorption-equilibrium is reached, subsequent cooling down and heating up should not lead to a new peak in N_2O-emissions. So the second peak might indicate that formation of adsorbed N_2O continues during the cooling down period.

Consequently, the increased N_2O-emissions that are observed for SCRdeNO_x might still be caused by low temperature formation of adsorbed N_2O, followed by high temperature desorption. This also might explain why the subsequent peaks in N_2O-emissions are smaller than the first one.

This theory of adsorption in a lower temperature window, and desorption at higher temperature levels certainly complicates the translation of the stationary 13-mode test results into a real-life emission factor.

Cold start N_2O-emissions

For some of the vehicles that were tested, an additional test was performed with a cold engine. 'Cold' means that the oil and cooling liquid temperatures are at 22 °C when the test is started, while in a 'hot' test the engine has been given sufficient time to let the temperatures stabilise at a specified engine load.

The results showed no significant changes in the N_2O-emissions, in comparison with the 'hot' test. Therefore the conclusion seems justified that N_2O-emissions for HD vehicles can not be seen as a cold start problem (as is concluded for passenger cars with three-way catalysts), but that they are rather independent of the starting temperature.

5 Real-life N_2O-emissions

5.1 Introduction

With the many results and data analysis available from the previous chapter, the next step is to convert these into real-life emission factors. At first for the time period between 1995 and the present, and then extrapolated to the object period from 1988 until 2010. The large number of test results will ensure that, compared to earlier studies and test programmes, much better founded emission factors for N_2O can be derived. Still, this conversion is not as straightforward as it may look. There are quite a number of factors that will introduce inaccuracies into such a conversion. The most important ones are given here:

- The measurements have been performed with a steady-state test. In practice however, the engine is operated only in transient conditions. A steady-state emission factor may therefore not be seen as an objective reflection of what would be emitted during real-life conditions (see also *Test inaccuracies* in Paragraph 4.2). Furthermore, these 'real-life conditions' will be different for each individual vehicle, depending on the vehicle application, driver, loading condition, road profile, surrounding traffic etc. Therefore, a real-life emission factor can at best only be a good indication of what might be expected in real-life conditions.
- The g/kWh emission factor determined over the 13-mode test is related to the energy delivered by the engine. A real-life emission factor is presented as a g/km value. Therefore, a conversion factor has to be found that accounts for the average energy needed to cover a distance of one km. Again, this conversion factor is depending on vehicle and driving characteristics.
- The data analysis has shown that the temperature of the catalyst plays a very important role in the N_2O formation. The temperature fluctuations within the test will therefore have been very determining for the test result. Obviously, the temperature pattern during real-life conditions will look different.
- The demonstrator vehicles within the measurement programme have experimental after-treatment systems, which not necessarily have the same technology and calibration as the future production vehicles they precede. This introduces an extra uncertainty for Euro 4 and Euro 5 emission factors.

5.2 Approach

The translation of the N_2O-emission results from the 13-mode tests is performed as follows. First of all the methodology of Adapted Weighting Factors is applied [4]. The idea behind this method is to replace the 'standard' weighting factors applied for the 13-mode tests by weighting factors that have been derived from a driving cycle which is representative for the driving situation that is investigated. Multiplying the adapted weighting factors with the individual emission results on the 13 modes delivers the emission factor for this driving situation. For emission components that are not very sensible for transient engine conditions, this is a reasonable approach.

Real-life driving cycles

Over the last years, TNO has gained experience in the development of driving cycles and emission factors representative for real-life conditions. For the project *HD Testcycles*, a set of representative testcycles was developed for different road types, vehicle masses and driving conditions [5]. They provide the best resemblance with

average driving conditions of HD vehicles in the Netherlands, though there is still a need for more data to further validate the testcycles. Using an interpolation routine, the adapted weighting factors are found for these cycles and emission factors are derived. As the energy delivered by the engine and the distance in km of the cycles are known, the emission result can be converted into a g/km emission value. Table 5.1 shows the characteristics of the cycles that are selected for the calculation.

Cycle nr.	File	kW/tonne	Roadtype	Traffic	$v_{average}$ [km/h]	RPA [m/s^2]
1	ST07-20A	7	urban	average	24.7	0.139
2	BU07-40C	7	rural	average	40.1	0.099
4	SN07-85B	7	highway	average	83.3	0.031
5	ST12-20A	12,5	urban	average	20.0	0.174
6	BU12-40B	12,5	rural	average	40.0	0.126
8	SN12-85B(new)	12,5	highway	average	81.0	0.049

Table 5.1 – Characteristics of representative HD vehicle testcycles

The vehicle loading is indicated by the parameter kW/tonne. This is the ratio of rated engine power, divided by actual weight (empty mass plus load). This factor has a high influence on the testcycle; for low kW/tonne values the average load within the testcycle is higher, as well as the conversion factor (kWh/km), if the same vehicle is observed. Average traffic conditions means that the testcycle is representative for average dynamic behaviour of the traffic. The Relative Positive Acceleration (RPA) is a relevant indicator for this dynamic behaviour. For more information on this topic please refer to [5].

Vehicle categories

Annually, TNO provides a set of emission factors to RIVM, the national Dutch institute for research of public health and environmental issues. This inventory uses a vehicle categorisation in 5 different classes, with specified gross vehicle weight (GVW) and loading factor.

For the overview of N_2O-emission factors in this report it is aimed to basically use the same categories. The rated engine power is not specified for these vehicle classes, so another source had to be used to supply this information. Recently a new version has been published of the Handbook Emission Factors, a common initiative by the environmental governments of Germany, Austria, and Switzerland to determine real-life emission factors [6]. The power-to-weight ratio of the closest vehicle class was used to determine the rated power for the vehicle classes in this report.

The HD testcycles have been developed for the heavier HD vehicle categories. This is reflected in the kW/tonne values, which are on the low side. Especially the lighter trucks are usually somewhat overpowered, so for this category these testcycles can only predict emission factors for fully loaded vehicles. Additionally, the GVW of the vehicle categories had to be adjusted slightly in order to let the GVW coincide with the rated power and the kW/tonne ratio.

Table 5.2 presents the vehicle categories that have been selected, which resemble the categories for the annual emission inventory as close as possible.

Vehicle type	GVW [tonne]	Load condition	Actual weight [tonne]	Power to mass [kW/tonne]	Rated power [kW]
Light truck	6.8	fully loaded	6.8	12.5	85
Medium truck	13.6	fully loaded	13.6	12.5	170
Heavy truck	37.1	half loaded	20.8	12.5	260
Heavy truck	37.1	fully loaded	37.1	7	260
Truck with trailer/semitrailer	40.0	half loaded	22.4	12.5	280
Truck with trailer/semitrailer	40.0	fully loaded	40.0	7	280
Urban bus	15.2	fully loaded	15.2	12.5	190

Table 5.2 – HD vehicle categories selected for calculation of N_2O-emissions.

5.3 Emission factors

Based on the results from the measurements and the adapted weighting factors for the HD testcycles, emission factors have been calculated for the defined vehicle categories. The results are presented in Table 5.3, for the engine technologies that have been investigated in this project. The emission factors for the demonstrator vehicle with EGR and CRT as well as the lean-burn CNG vehicle are not specified separately. They are of the same order of magnitude as the Euro 3 vehicles. The result for the stoichiometric CNG vehicle is not presented, since the measurements on this particular engine can not be considered to be representative for this technology class (see also Appendix D). The N_2O-emission level will probably lie between the 'Euro 3' and 'SCRdeNOx' categories

These results give the impression that N_2O-emissions have been calculated with quite good accuracy. However, the inaccuracies in the test results (Paragraph 4.2) and restrictions of the methodology to calculate real-life emissions (Paragraph 5.1) have to be respected. It is difficult to estimate the absolute accuracy of the N_2O-emission values taking all these aspects into account, but it is expected that the real N_2O-emissions could very well be 25% higher or 50% lower, especially for the emissions in the lower ranges. The difference in positive and negative accuracy is caused by the cross-sensitivity of the analyser for CO_2-emissions. For that reason, the engine technologies with almost zero emission have their result presented as a 'lower than …' value.

Euro 1 Vehicle type	GVW [tonne]	Load condition	N_2O emissions [mg/km] Urban	Rural	Highway
Light truck	6.8	fully loaded	< 6	< 5	< 3
Medium truck	13.6	fully loaded	< 11	< 9	< 7
Heavy truck	37.1	half loaded	< 17	< 14	< 10
Heavy truck	37.1	fully loaded	< 19	< 16	< 11
Truck with trailer/semitrailer	40.0	half loaded	< 18	< 15	< 11
Truck with trailer/semitrailer	40.0	fully loaded	< 20	< 17	< 11
Urban bus	15.2	fully loaded	< 12	< 10	< 7

Euro 2 Vehicle type	GVW [tonne]	Load condition	N_2O emissions [mg/km] Urban	Rural	Highway
Light truck	6.8	fully loaded	< 5	< 5	< 3
Medium truck	13.6	fully loaded	< 11	< 9	< 6
Heavy truck	37.1	half loaded	< 17	< 14	< 10
Heavy truck	37.1	fully loaded	< 18	< 16	< 10
Truck with trailer/semitrailer	40.0	half loaded	< 18	< 15	< 10
Truck with trailer/semitrailer	40.0	fully loaded	< 20	< 17	< 11
Urban bus	15.2	fully loaded	< 12	< 10	< 7

Euro 3 Vehicle type	GVW [tonne]	Load condition	N_2O emissions [mg/km] Urban	Rural	Highway
Light truck	6.8	fully loaded	< 3	< 3	< 2
Medium truck	13.6	fully loaded	< 5	< 5	< 4
Heavy truck	37.1	half loaded	< 8	< 8	< 6
Heavy truck	37.1	fully loaded	< 10	< 9	< 7
Truck with trailer/semitrailer	40.0	half loaded	< 9	< 9	< 7
Truck with trailer/semitrailer	40.0	fully loaded	< 11	< 10	< 7
Urban bus	15.2	fully loaded	< 6	< 6	< 5

SCRdeNOx Vehicle type	GVW [tonne]	Load condition	N_2O emissions [mg/km] Urban	Rural	Highway
Light truck	6.8	fully loaded	18	24	21
Medium truck	13.6	fully loaded	36	49	41
Heavy truck	37.1	half loaded	55	75	63
Heavy truck	37.1	fully loaded	89	93	69
Truck with trailer/semitrailer	40.0	half loaded	59	81	68
Truck with trailer/semitrailer	40.0	fully loaded	96	100	74
Urban bus	15.2	fully loaded	40	55	46

CRT Vehicle type	GVW [tonne]	Load condition	N_2O emissions [mg/km] Urban	Rural	Highway
Light truck	6.8	fully loaded	19	14	9
Medium truck	13.6	fully loaded	38	29	17
Heavy truck	37.1	half loaded	58	44	26
Heavy truck	37.1	fully loaded	59	41	24
Truck with trailer/semitrailer	40.0	half loaded	63	47	28
Truck with trailer/semitrailer	40.0	fully loaded	64	44	25
Urban bus	15.2	fully loaded	43	32	19

Table 5.3 – Calculated real-life N_2O-emission factors for different HD engine technologies

N_2O-emissions from 1988 to 2010

With the inventory of N_2O-emissions for different HD engine technologies completed, the projection over the objected period from 1988 to 2010 can be made. The main conclusion from Table 5.3 is that the N_2O-emission for conventional engine technologies (i.e. without after-treatment) is almost zero, or at least never more than 20 mg/km. According to Paragraph 2.2, after-treatment systems will not be used on HD engines until the Euro 4 emission limits apply. For new vehicle types to be introduced this will be from October 2005, while one year later the limits apply for all vehicles sold in the EU. The general idea is that SCRdeNOx systems will be mainly used to fulfil the Euro 4 standards, as well as for Euro 5 (applicable from October 2008 for new vehicle types, and October 2009 for all vehicles sold). For some specific applications (e.g. urban buses, or vehicles wit smaller engines) cooled EGR combined with a CRT filter could be an alternative. CNG technology is not expected to achieve a substantial market share until 2010. In terms of N_2O-emissions, the highest contribution of N_2O can be expected from SCRdeNOx after-treatment. So, if the projection is made for Euro 4 vehicles exclusively equipped with SCRdeNOx systems, this can be seen as the maximum scenario (Scenario 1 in Figure 5.1). A second scenario has been added as well, where the assumption is made that 20% of the vehicles have EGR and a CRT filter (based on the demonstrator vehicle), while the other 80% has a SCRdeNOx system installed.

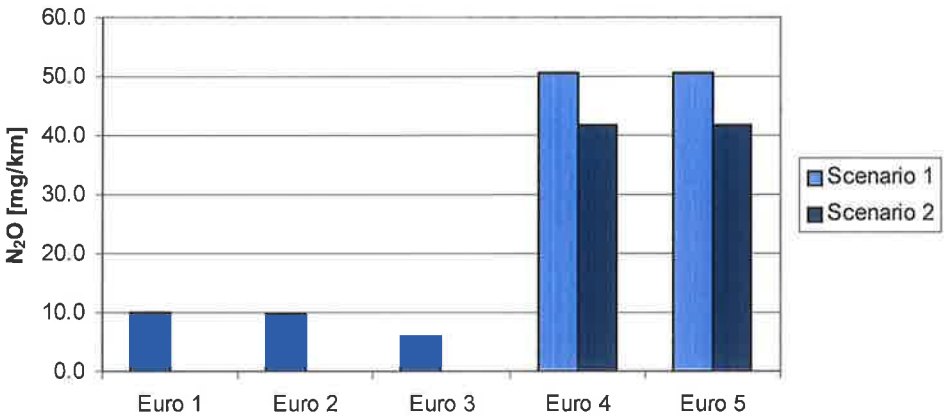


Figure 5.1 – Real-life N_2O-emission factors for different HD engine technologies, for 2 scenario's (1 - 100% SCRdeNOx after-treatment, 2 – 80 % SCRdeNOx and 20% cooled EGR with CRT filter)

As can be seen from Figure 5.1, the N_2O-emission of present-day HD vehicles (Euro 1 to 3) is well below the value of 30 mg/km assumed by the IPCC. Beyond 2005, when exhaust after-treatment will be used to meet the Euro 4 and 5 emission limits, the N_2O-emission or trucks and buses is expected to rise significantly to a value even higher than the IPCC value. However, expressed in CO_2-equivalents this value represents only 15 gCO_2/km at maximum, which is less than 2% of the direct CO_2-emission of HD vehicles (about 820 g/km if the same weighing is applied).

The effect of these calculated emissions on the level of national N_2O-emissions falls outside of the scope of this project. However, a rough estimation has been made, by using statistical data from the Dutch statistical bureau (CBS) [7], the national institute of public health and environment (RIVM) [8], and information that was available internally. To make this emission projection, information had to be provided on the following aspects:

- Level and growth of total HD vehicle fleet per year over the projected period
- Level and growth of sold vehicles per year over the projected period
- HD vehicle type distribution within the vehicle fleet (using the categories specified in Table 5.2)
- Road type distribution (distance covered on urban roads, rural roads and highways.
- Annual mileage of HD vehicles

For reference purposes, the calculation method as well as the assumptions on the above mentioned aspects have been summed up in Appendix E.
It may be evident that not all information was available at the detailed level that is needed for an accurate projection. Therefore, the result can only be treated as indicative. The emission projection for the Netherlands between 1988 and 2010 in ktonnes of N_2O is shown in Figure 5.2.

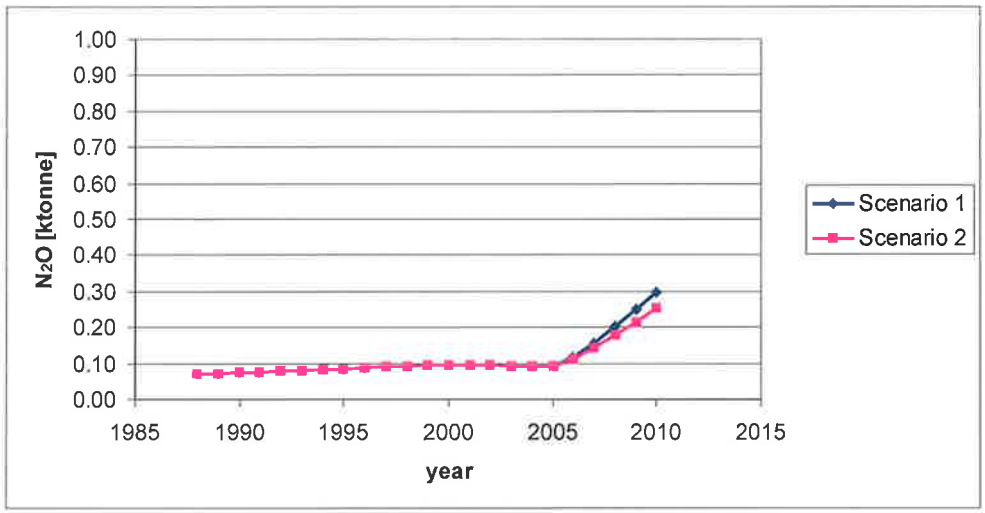


Figure 5.2 – Indicative N_2O-emission projection of HD vehicles for the period between 1988 and 2010 in the Netherlands.
(for scenario description refer to Figure 5.1)

The indication from Figure 5.2 is that the N_2O levels have always been at a very low level, and that as of Euro 4 the tendency is a firm rise in emissions. Still, the absolute level remains rather low. Beyond 2010 the N_2O-emission is expected to keep rising, as the pre-Euro 4 engines are being replaced by engine technologies with after-treatment. In this projection, about 39 % of the vehicle fleet exists of Euro 4 or higher engine technology in 2010.

5.4 Policy aspects for the Dutch situation

Before the policy aspects are outlined for the Dutch situation concerning N_2O-emissions of HD vehicles, it must be explicitly stressed here that these are meant as *technical information* from the authors towards the environmental authorities.

The study on N_2O-emissions of Heavy Duty vehicles was preceded by a similar programme for passenger cars. The passenger car study showed an overestimation of national N_2O-emissions by both the Dutch and the (more recent) IPCC default factors. After conducting the underlying investigation, a similar conclusion can be drawn for HD vehicles. However, where in case of passenger cars N_2O-emissions

will drop in time due to ongoing technological developments, N_2O-emissions from HD vehicles most probably will increase due to these developments.

Table 5.4 presents changes in national annual reports on N_2O-emissions over the years, according to the developments in new insights.

Dutch annual N_2O emissions from road transport in ktonne/year								
Calculatory bases	*Dutch estimate*		*IPCC*		*IPCC corrected*		*TNO predictions*	
National reporting year	1999		2000		2001		2005	2010
Year of calculation	1990	1998	1990	1999	1990	2000	2003	2003
Passenger cars	3.2	3.8	2.3	3.1	0.7	1.3	0.6	0.3
Light duty vehicles	0.2	0.3	0.2	0.4	0.1	0.3	<0.1	<0.1
Heavy Duty vehicles	2.1	1.8	1.9	1.5	0.2	0.2	0.1	0.3
Two wheelers	0.0	0.0	0.0	0.0	0.0	0.0	?	?
Total Dutch road transport	**5.5**	**5.9**	**4.4**	**5.0**	**1.0**	**1.9**	**+/- 0.7**	**+/- 0.6**

Source 1999, 2000, 2001: [8] [10]
2003: TNO-Automotive

Table 5.4 – Changes in national N_2O-emissions as a result of developing insights

This table shows that due to evolving IPCC insights, the annual Dutch road transport N_2O-emissions estimate has been adjusted from 5.9 ktonne for 1998 to 1.9 ktonne for 2000. Based on recent measurements, TNO predicts an even further drop in the estimate to about 0.7 ktonne in 2005. Without further legislative action, TNO foresees that between 2005 and 2010 the annual N_2O-emission from road transport will probably stabilise at about 0.6 to 0.7 ktonnes, with a tendency to further increase beyond 2010. This stabilisation is the result of further decreasing N_2O-emissions from passenger cars in combination with the increase in N_2O-emissions from HD vehicles due to the application of catalyst technology (mainly SCRdeNOx systems). Beyond 2010, the HD vehicle related N_2O-emissions will still rise, since in that year some 60% of the fleet has yet to be replaced by Euro 4 or higher engine technology. Starting the same year, HD vehicles will be responsible for more than 50% of the Dutch road transport N_2O -emissions.

The gathered new insights regarding the causes and magnitude of N_2O-emissions of traffic have consequences for the Dutch policy towards this emission component; the predicted low level of absolute N_2O-emissions in 2010 should not be considered a motivation not to take action to further reduce these emissions. Since N_2O is a strong greenhouse gas, national policy should not be based on N_2O mass emission targets only, but also addresses the CO_2-equivalent of N_2O-emission.

The CO_2-equivalent from N_2O-emission of HD vehicles in 2003 is about 30 ktonne (TNO estimate). To put this in perspective: the total CO_2-emission of all road traffic in the Netherlands for 2001 was 32.0 Mtonne [8], so N_2O-emissions of HD vehicles add 0.1% to the total Dutch road transport CO_2-emissions over this year. By 2010 the N_2O related CO_2-contribution could increase by a factor of 3 (to 0.3%), in case all new vehicles sold after 2005 are equipped with a SCRdeNOx system.

In assessing the contribution to the greenhouse effect of a particular engine technology, it will not suffice to only observe the direct N_2O-emissions. The fuel consumption (and therefore the direct CO_2-emission as well) can also vary from one engine technology to the other. For example, the direct N_2O-emissions of vehicles with an EGR/CRT system are found to be lower than for those with a SCRdeNOx system installed. However, the fuel consumption may be some 2 to 3 % higher [9], diminishing the effect of less emitted N_2O in the global warming potential (2% of CO_2-equivalent at maximum according to Paragraph 5.3).

The large potential increase of N_2O-emissions due to the implementation of emission control systems, will ask for more and frequent monitoring of this component in the future.

6 Conclusions

In an elaborate measurement programme the N_2O-emissions of HD vehicles have been measured, and factors influencing these emissions have been assessed. For engine technologies used to comply with Euro 1 to Euro 3 standards, the N_2O-emissions predicted for real-life conditions were found to be much smaller than the assumed value used by the IPCC (<10 mg/km versus 30 mg/km). Based on the test results, for after-treatment systems such as urea SCRdeNOx and EGR combined with a CRT filter that will be used to fulfil the emission requirements of Euro 4 and 5, a strong increase in N_2O-emissions up to 50 mg/km is expected. However, in terms of CO_2-equivalents the resulting levels can still be considered quite small (less than 2% of the direct CO_2-emission).

A rough indication of the national N_2O-emission by HD vehicles in the Netherlands was made. This showed that over the object period the absolute emission level would increase from 0.07 ktonne in 1988 to some 0.30 ktonne in 2010. In terms of CO_2-equivalents this means an increase from 21 to 87 ktonnes (for reference purpose: the total road traffic related CO_2-emission in the Netherlands over 2001 amounted to 32.0 Mtonne).

The assumed correlation between NO_x and N_2O-emissions has been assessed on the basis of the measurements, but could not be established. The conclusion of this assessment was that a higher NO_x-emission *may lead* to higher N_2O-emission, but that a higher N_2O-emission is *not the result of* an increase in NO_x-emission. Various other aspects play at least an equally important role, such as exhaust gas temperature and catalyst composition. Dedicated N_2O measurements will therefore remain necessary if an emission factor for N_2O is needed.

In this report, quite a number of inaccuracies and uncertainties related to the measurement set-up and the chosen calculation approach have been summed up. Consequently, the results obtained for the emission factors cannot be seen as an absolute matter of fact. Within the boundary conditions of testing methods, analyser specifications, and availability of data on vehicles and driving conditions, the authors have tried to come up with the best representative results possible. Nevertheless, a large uncertainty margin needs to be taken into consideration, especially for the emission factors in the lowest ranges. There are several indications that the actual N_2O-emission in real-life might be lower than the values indicated in this report, leading to an asymmetric uncertainty margin, roughly estimated at plus 25% and minus 50%.

7 References

1. Gense, N.L.J. and Vermeulen , R.J., *N_2O formation in vehicle catalysts*, TNO-report 02.OR.VM.017.1/NG, Delft, February 2002
2. Feijen-Jeurissen M., Oonk H., Gense N., N_2O-emissions from mobile sources – Impact of technology development, report R2001/113, TNO-MEP, Apeldoorn, the Netherlands (2001)
3. G. Leclerq, L. Leclerq, C. Dathy, J.F. Lamonier, P. Malfoy, M. Prigent, G. Mabilon, Proc. 6th Int. Workshop on Nitrous Oxide Emissions 1994, Turku Finland, p.437.
4. Dr. Ir. C.J.T. van de Weijer, *Heavy-Duty Emission Factors*, Oktober 1997, Delft
5. Riemersma, I.J. and Hendriksen, P., *Update and Evaluation of HD Testcycles*, TNO report 00.OR.VM.081.1/IJR, June 2001, Delft
6. Hausberger, S., *Update of the Emission Functions for Heavy-Duty vehicles in the Handbook Emission Factors for Road Traffic (2nd draft)*, October 2002, Graz
7. Statline – online statistics from the CBS website (www.cbs.nl)
8. Brink, R.M.M. van der, *Verkeer en Vervoer in de Milieubalans 2000*, RIVM rapport 251701044, December 2000, Bilthoven
9. Verbeek, R. et al., *DAF Euro-4 heavy duty diesel engine with TNO EGR system and CRT particulates filter*, SAE paper 2001-01-1947, 2001, Delft
10. Taakgroep Verkeer en Vervoer CBS/RIVM/RIZA/TNO, *Methoden voor de berekening van de emissies door mobiele bronnen in Nederland, Rapportagereeks MilieuMonitor Nr. 4*, January 2002, Voorburg/Bilthoven/Lelystad/ Delft/Apeldoorn
11. IPCC, http://www.grida.no/climate/ipcc_tar/wg1/248.htm (2001)

8 Nomenclature

CRT	Continuous Regenerating Trap (specific diesel particulate filter type)
ECE R49	Reference name for the conventional 13-mode test (up to Euro 2)
EGR	Exhaust Gas Recirculation system
ESC	European Steady-state Cycle (13-mode test for Euro 3 and beyond)
ETC	European Transient Cycle
FP5	Framework Programme 5
GVW	Gross Vehicle Weight
GWP	Global Warming Potential
HD	Heavy Duty (vehicles with >3.5 tonnes GVW)
IUC	In-Use Compliance
IUE	In-Use Emissions (focuses on emission factors, but also IUC aspects)
LD	Light-Duty (vehicles with <3.5 tonnes GVW)
SCRdeNOx	Selective Catalytic Reduction system to reduce NO_x-emissions
VROM	Dutch acronym for "Spatial planning, Housing and the Environment"

A Update of the literature review

A literature survey was performed, in an attempt to fully cover all relevant publications on N_2O-formation and emissions in SCRdeNO$_x$ and CRT-systems, published in the period after the literature review by Feijen et al.[1] was performed (period summer 2000 to 2002).

Relevant chemical en chemical engineering Journals were surveyed through Pica-on-line, using the following key-words:

Key-word	***Number of hits***
N_2O	*(493)*
N_2O diesel	0
N_2O SCR	20
N_2O emission	35
N_2O CRT	0
N_2O review	1
Diesel catalyst	71
Nitrous oxide	*(540)*
Nitrous oxide diesel	0
Nitrous oxide SCR	3
Nitrous oxide emission	56
Nitrous oxide CRT	0

On top of that, SAE-papers and Dieselnet were surveyed using the search terms 'N_2O' and 'nitrous oxide'. This led to an additional 2, respectively 17 hits.

The abstracts of all articles were studied (except for the hits in brackets: for N_2O and nitrous oxide in Pica-on-line). On the basis of these abstracts most of the articles could be rejected for obtaining relevant information. For 21 articles it was difficult to learn from the abstract whether the article could contain relevant information; these articles were ordered and checked for additional information on relevant topics.

The result of the literature survey did not lead to new insight into the matter of N_2O-formation. On the other hand, the extra information did support the statements made in the earlier performed review.

[1] Feijen-Jeurissen M., Oonk H., Gense N., N_2O-emissions from mobile sources – Impact of technology development, report R2001/113, TNO-MEP, Apeldoorn, the Netherlands (2001)

B Principles of (catalytic) technologies for diesel engines and the influence on N_2O-emission

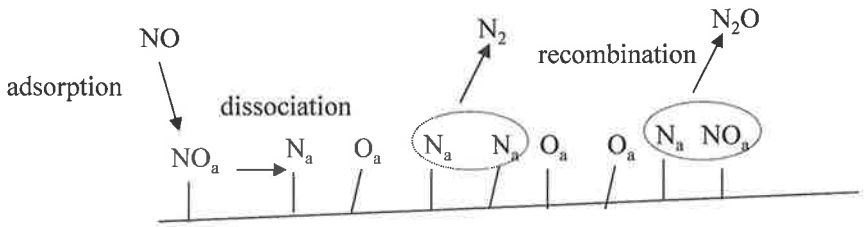
B.1 Introduction

Diesel emissions, of which NO_x and particulate matter have the highest share, can be controlled either at their source, through engine design and combustion process modifications or by exhaust gas after-treatment using particulate filters or catalysts. Several technologies, mainly catalytic exhaust gas after-treatment systems, and their influence on the N_2O-emission are explained in the following subsections.

B.2 N_2O-formation on Rh-containing catalysts

N_2O can be formed as a by-product of NO-reduction over certain active metals. This process is well investigated for the rhodium-centra (Rh) in three-way catalysts, but may proceed as well over other metals as platinum (Pt) and palladium (Pd), as present in diesel after-treatment technology.

N_2O-formation over Rh
The mechanism of nitrous oxide formation on three-way catalysts is nowadays well understood and is simplified in Scheme B.1. At low temperatures NO is adsorbed (indicated as NO_a), but NO_a-dissociation (into N_a and O_a) is slow and the catalyst surface is covered with high concentrations of NO_a. At high temperatures the NO_a-dissociation process is very fast, so N_a and O_a will prevail. However at intermediate temperatures moderate rates of dissociation may lead to neighbouring pairs of NO_a and N_a, capable of forming N_2O.



Scheme B.1 - Simplified mechanism of NO-decomposition and N_2O-formation

Scheme B.1 suffices to understand a number of trends in N_2O-emissions. To name a few [1]:

- as explained above, the catalyst temperature plays an important role. There is vast experimental evidence that under ideal conditions (and at λ=1) N_2O-formation is negligible under 200 °C, reaches a maximum at about 280 °C, where at 350 °C N_2 is the dominant product. This renders nitrous oxide emissions from three-way catalysts to a cold-start problem (see Figure B.1).
- SO_2 in the exhaust-gas inhibits NO-dissociation, thereby shifting the temperature window in which NO_a and N_a exist next to each other to a higher temperature level.
- N_2O-formation increases when NO-concentrations increase. At increasing NO-concentration the NO-coverage of the catalyst surface will be higher, so there will be more neighbouring NO_a-N_a-pairs, that might form N_2O.

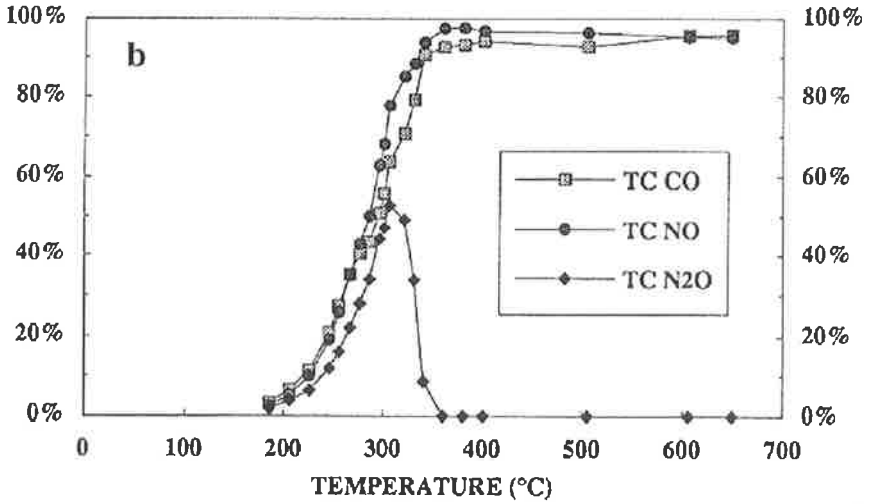


Figure B.1 - NO reduction with CO over a three-way catalyst (TC, 1%Pt-0.2%Rh/Al_2O_3); conversion of NO and CO and the formation of N_2O vs. temperature [2].

N_2O-formation over Pt and Pd

N_2O-formation on Rh-based catalysts as the three-way catalyst has been studied extensively. There are numerous indications that similar reaction progress as well over platinum (Pt) and palladium (Pd), so catalysts based on these materials are suspected to also produce N_2O.

The mechanism of N_2O-formation over Pt and Pd resembles the mechanism of N_2O-formation over Rh. At low temperatures a large amount of NO molecules is adsorbed at the surface, and upon NO conversion N_2O can be formed by the reaction of adsorbed NO and N-atoms at the catalyst surface. At high temperatures a dissociative adsorption of oxygen occurs. As a result the activity of the catalyst changes at increasing temperatures: NO adsorption and conversion is inhibited; NO will be oxidised to NO_2 rather than being reduced (to N_2 and N_2O) and hydrocarbons will be oxidised in a non-selective oxidation way [3].

There are several reports of N_2O-formation over Pt-containing catalysts:

- Matsuoka et al. investigated the performance of a *platinum catalysed soot-filter*. They examined the regeneration by NO of a supported platinum catalyst on which soot was deposited by the cracking of n-dodecane prior to the reaction with NO. Above 400°C NO and the deposited soot could be completely converted, but between 250°C and 400°C N_2O-formation was observed (up to 10%) [4]. In addition, research concerning the selective catalytic reduction of NO by hydrocarbons over platinum catalysts and with respect to the NO_x-storage catalyst show that over a platinum catalyst under lean reaction conditions, high amounts of N_2O can be formed during the NO_x-reduction by hydrocarbons. Based on these results, it is expected that N_2O can be formed in platinum catalysed particulate filters such as the CRT and the CSF.
- There are many reported cases of *reaction of NO and hydrocarbons (HC-SCR)* over platinum catalysts at relatively low temperatures (200 °C-250 °C) where a very large amount of N_2O is produced [5]. The selectivity towards N_2O-formation often easily reaches 70% and goes in extreme cases up to 100% [6]. At increasing temperatures the hydrocarbons preferentially react with O_2 and the NO_x-conversion decreases. Consequently, the NO conversion efficiency can only be sustained over a relative narrow temperature window. While at low temperature N_2O is observed as by-product, at high temperature NO_2 is found [5,6]. The product selectivity over platinum catalysts (N_2O / N_2) was found to depend on the type of

reductant. In the case of SCR with propane or ethene significant emission of N_2O occurred. On the other hand, no N_2O was produced in the case of SCR with toluene. Many hydrocarbons have been tested, and toluene was found to be unique in this effect. It seemed possible that the aromatic character of toluene could be important [4, 6].

- In addition, Lörch and Weisweiler [7] reported for *the NO_x-storage catalyst* (which also contains platinum) that under lean conditions and between 150 °C and 350 °C NO_x is partly converted into N_2O rather than N_2.

There is no evidence of N_2O-emissions from Pd-catalysts; however similarities in the chemical character of these components indicate N_2O formation must be possible here as well.

N_2O-formation over other noble metal catalysts
Besides supported noble metal catalysts, other catalysts for the selective NO_x-reduction under oxidising conditions have been widely studied. The famous examples of these catalysts are Cu-ion exchanged zeolites and base metals supported on alumina. But these catalysts have many problems for practical use such as low NO_x-conversion, a narrow temperature window and insufficient durability and thermal stability. N_2O-formation over these catalysts is often lower than found for the platinum catalysts, but depends very much on the specific catalyst composition and reaction conditions [8, 9, 10, 11].

B.3 In-cylinder measures

The N_2O-emission formed during the combustion process itself is very low. According to Hendriksen [12], the engine-out N_2O-emission of a HD diesel engine is about 0.03 g/kWh. It is expected that technologies such as 4 valves per cylinder, advanced high-pressure injection systems and EGR have no significant effect on the engine-out N_2O. However, the engine out NO_x will change, e.g. direct injection induces a higher NO_x formation in the engine than indirect injection, while the application of EGR significantly reduces the NO_x formation in the engine. In combination with a catalytic after-treatment system, the changed NO_x concentration in the engine out gases could affect the N_2O-emission level. For NO_x-reduction over the three-way catalyst, indications are found that a higher engine out NO_x might result in higher N_2O levels in the exhaust gases (see also Paragraph B.2). This relationship should be further investigated.

B.4 Oxidation catalyst

This type of catalyst is designed for the oxidation of CO, HC and the VOC part of the particulate matter, and generally contains small amounts of platinum or palladium as the active species.
There is no specific information available about N_2O-emission from this catalyst, however N_2O-formation is expected over all platinum and palladium containing oxidation catalysts, which includes the oxidation catalyst.

B.5 Particulate filter

Diesel particulate emissions can be controlled by exhaust gas after-treatment using particulate filters. In this system the particulate matter is first captured and subsequently oxidised. The conventional traps for HD applications are regenerated by heating in air to oxidise the soot with O_2 at temperatures between 550 °C-600 °C [13]. More

advanced filters have been developed for regeneration of the filter at lower temperatures. These filters use a fuel additive or contain an oxidation catalyst. Dependent on the combination of the additive and the filter technology the minimum temperatures for regeneration are between 325 °C and 430 °C [14].

Catalysed soot filter
The particulate traps for HD applications, which could be used in 2005 and are already applied in certain fleets (especially buses for public transportation), are expected to be of the self-regenerative type, without the use of a fuel additive. This is only possible when using a low sulphur fuel, because platinum is an active catalyst for the oxidation of SO_2 into SO_3, which causes sulphate and H_2SO_4 formation. A catalysed filter uses one or more filters containing metals such as platinum, which are effective in oxidising carbon particulates. An example is the Catalysed Soot Filter (CSF) of Engelhard. The regeneration takes place in two ways, namely: platinum catalyses the direct soot oxidation with O_2, but also induces the oxidation of NO into NO_2, which is a much better oxidant for soot than either O_2 or NO [15]. The platinum filter regenerates at 350 ^{o}C and above, but suffers from sulphate formation [14, 16].

Continuous Regenerating Trap
A special category of particulate matter reduction technology is formed by the Continuous Regenerating Trap (CRT), which is developed by Johnson Matthey. It consists of a platinum based oxidation catalyst, upstream of the particulate filter trap. NO is oxidised over the platinum catalyst into NO_2, which subsequently regenerates the filter by reaction with the particulate matter. The CRT is effective in the region of 330 ^{o}C. Since the processes of particulate trapping and particulate destruction are continuous above these temperatures, the system is referred to as a Continuously Regenerating Trap (CRT).
This process is illustrated in the Figure B.2.

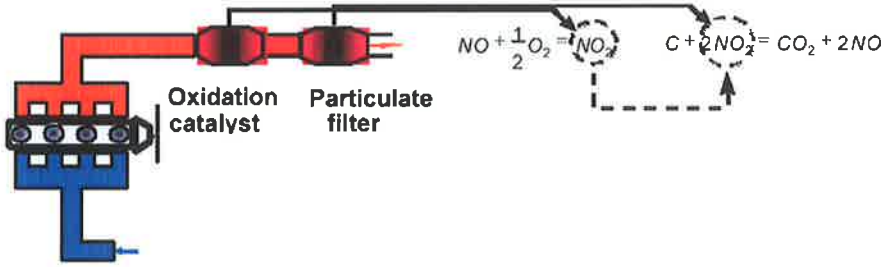


Figure B.2 – Schematic overview of processes within a CRT

Like the catalysed soot filter, the CRT technology is only applicable when using a low sulphur fuel, because platinum is an active catalyst for the oxidation of SO_2 into SO_3, which causes sulphate and H_2SO_4 formation. These compounds are also counted as particulate matter [13].
The most common application expected for CRTs is on HD vehicles, but also some passenger car manufacturers (including Volkswagen) consider the application of a CRT on their vehicles.

Possibility of N_2O-formation
There is not much known about the formation of N_2O over particulate filters. N_2O-formation is not expected for the conventional un-catalysed filters, which operate without fuel additives.

However, for platinum catalysed particulate filters such as the CSF and CRT some N_2O formation can be expected (see also Paragraph B.2).
The influence of the fuel additives probably very much depends on the type of metal additive. For the platinum containing additives N_2O-formation might be expected for the same reason as mentioned above. Based on knowledge from the three-way catalyst it can be mentioned that addition of cerium to the three-way catalyst does not seem to increase the conversion of NO into N_2O.

B.6 NH_3-SCR

The so-called selective catalytic reduction (SCR) process is based on the reduction of NO by NH_3, through the following (main) reaction:

$$4NO + NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

The NH_3 is added to the exhaust gas in the form of ammonia or urea. This process is well established and is widely applied for the abatement of nitrogen oxides from waste gases of stationary sources (e.g. power plants). The commonly used catalysts are based on V_2O_5-TiO_2 with addition of either WO_3 or MoO_3. The application for mobile sources, mostly HD, is illustrated in the Figure B.3.

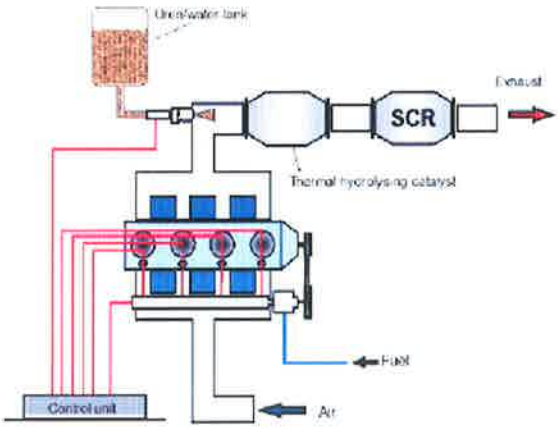


Figure B.3 – Schematic overview of SCRdeNOx system

In order to control the NO_x-reduction, ammonia or urea is injected into the flue gas prior to the catalyst. Urea is converted into NH_3 by thermal decomposition (into NH_3 + HNCO) and hydrolysis. Because the composition and the temperature of the exhaust gas strongly vary, a sophisticated control system is required.

Possibility of N_2O-formation
The vanadia-titania based catalysts are very active in the selective reduction of NO into N_2, but only in a restricted temperature window (depending on the exact catalyst composition about 350-450°C). At lower temperatures the NO_x-conversion is insufficient. Besides, with SO_2 containing exhaust gases, ammonium sulphate forms below 350 °C, which coats the downstream process equipment. At high temperatures (T>450 °C), NH_3 is oxidised non-selectively into NO_x and N_2O. Unlike NO, N_2O cannot be reduced by NH_3 under similar experimental reaction conditions. Although N_2O is formed at high temperatures (T>450 °C), the NO reduction is very selective towards N_2 within the optimum temperature window, where N_2O-formation is hardly observed.

SCR over vanadia on Titania catalysts has been extensively studied. Fundamental research showed that N_2O could be formed under certain reaction conditions, and very much depends on the reaction conditions and the catalyst composition. Topsøe et al. investigated the reaction selectivity under dry and wet conditions and found the formation of a considerable amount of N_2O under dry conditions, while in the presence of water the formation of N_2O is negligible [17]. This formation of N_2O in the medium temperature region proceeds most likely by the adsorption of NO on reduced vanadium-surface sites [18]. These sites are not likely to exist in the presence of water and oxygen, like typically present in exhaust gases. The selectivity also strongly depends on the catalyst composition. Contrary to the very selective conversion on NO over vanadia–titania catalysts, over bulk vanadia up to 15% conversion into N_2O is observed between 300 °C and 400 °C. Other catalysts, such as cerium and copper based catalysts, were also investigated for application in a broader or different temperature range, but generally show less activity or selectivity.

Havenith and Verbeek [16] investigated the N_2O-emission from HD diesel engines and the influence of a vanadium-titania urea SCR after-treatment unit. The engine out N_2O-emission of HD diesel engines typically ranges at very low levels of about 3 ppm. Urea-SCR over the vanadia-titania catalyst for HD diesel engines was active between 250-450 °C with a maximum NO_x-conversion at 350 °C. The results showed that the SCR catalyst has virtually no influence on the N_2O-emission.

B.7 NH_3-clean-up catalyst

Some of the ammonia injected by the SCRdeNOx system remains unreacted and is vented to the atmosphere (ca. 5-10 ppm NH_3). Therefore an oxidation catalyst may be applied downstream the SCR unit. Havenith and Verbeek measured the N_2O-emission and observed that when this platinum catalyst was applied the N_2O concentration increased to about 11-20 ppm: NH_3 was oxidised into N_2O and NO_x [16]. The first step in NH_3-oxidation is most likely through conversion of NH_3 to adsorbed NO species [19]. N_2O-formation can be explained by dissociation of NO and recombination to N_2O, similar to the mechanism in Scheme 1 (see Paragraph B.2). The reaction is expected to proceed at the same temperature interval as the formation of N_2O from NO (at about 200-300 °C).

B.8 References

[1] Feijen-Jeurissen M., Oonk H., Gense N., N_2O-emissions from mobile sources – Impact of technology development, report R2001/113, TNO-MEP, Apeldoorn, the Netherlands (2001)

[2] G. Leclerq, L. Leclerq, C. Dathy, J.F. Lamonier, P. Malfoy, M. Prigent, G. Mabilon, Proc. 6th Int. Workshop on Nitrous Oxide Emissions 1994, Turku Finland, p.437.

[3] G.P. Ansell et al. Appl. Catal B 10 (1996) 183-201

[4] K. Matsuoka, H. Orikasa, Y. Itoh, P. Chambrion, A. Tomita, Appl. Catal. B 26 (2000) 89-99

[5] M. Schneider, H. Lörch, W. Weisweiler, Chemie Ingenieur Technik (70) (1998) 570-574

[6] R. Burch, D. Ottery, Appl. Catal. B 9 (1996) L19-L24

[7] H. Lörch, H. Weisweiler, Chemie Ingenieur Technik (70) 6198, 749-753 (1998)

[8] P.J. van den Brink, C.M. McDonald, Appl.Catal. B 6 (1995) L97-L103

[9] N. Takahashi, Catal. Today 27 (1996) 63-69 (Toyota)

[10] T. Maunula, J. Ahola, H. Hamada, Appl. Catal. 26 (2000) 173-192

[11] B.J. Adelman, T. Beutel, G.D. Lei, W.M.H. Sachtler, Apll. Catal. B 11 (1996) L1-L9

[12] P. Hendriksen, P. de Koning, FTIR Measurements of N_2O emission from heavy-duty diesel engine, internal TNO report (1994)

[13] J.P. Warren, R. Allanson, P.N. Hawer, A.J.J. Wilkins, ImechE, 1998 S491/006

[14] S.J. Jelles, M. Makkee, J.A. Moulijn, G.J.K. Acres, J.D. Peter-Hoblyn, SAE paper 1999-01-0113

[15] R. Giles, N.W. Cant, M. Kögel, T. Turek, D.L. Trimm, Appl. Catal. B 25 (2000) L75-L81

[16] C. Havenith, R.P. Verbeek, SAE970185

[17] N. Topsøe, T. Slabiak, B.S. Clausen, T.Z. Srnak, J.A. Dumesic, J. Catalysis 34 (1992) 742-746

[18] V.I. Parvalescu, P. Grange, B. Delmon, Catalysis Today 46 (1998) 233-316
L. Gang, B.G. Anderson, J. van Grondelle, R.A. van Santen, W.J.H. van Gennip, J.W. Niemantsverdriet, P.J. Kooyman, A.Knoester, H.H. Brongersma, J. Catal., 206

C Measurements details

The testing method for the measurement of N_2O is in principle the same as used in the *In-Use Compliance Programme for Trucks*. The trucks are tested on a chassis dynamometer for gaseous emission, particulate emission and smoke emission, according to Directives 88/77/EEC (or Directive 1999/96/EC for Euro 3, 91/542/EEC and 72/306/EEC respectively. Though officially the tests have to be performed at an engine testbed, TNO has developed a method to simulate this test on a chassis dynamometer. The power losses between the engine and the wheels are calculated by formulae developed in the *Diesel Controle Methode* programme [1]. The inaccuracy of this methodology has been proven to be 4% at maximum.

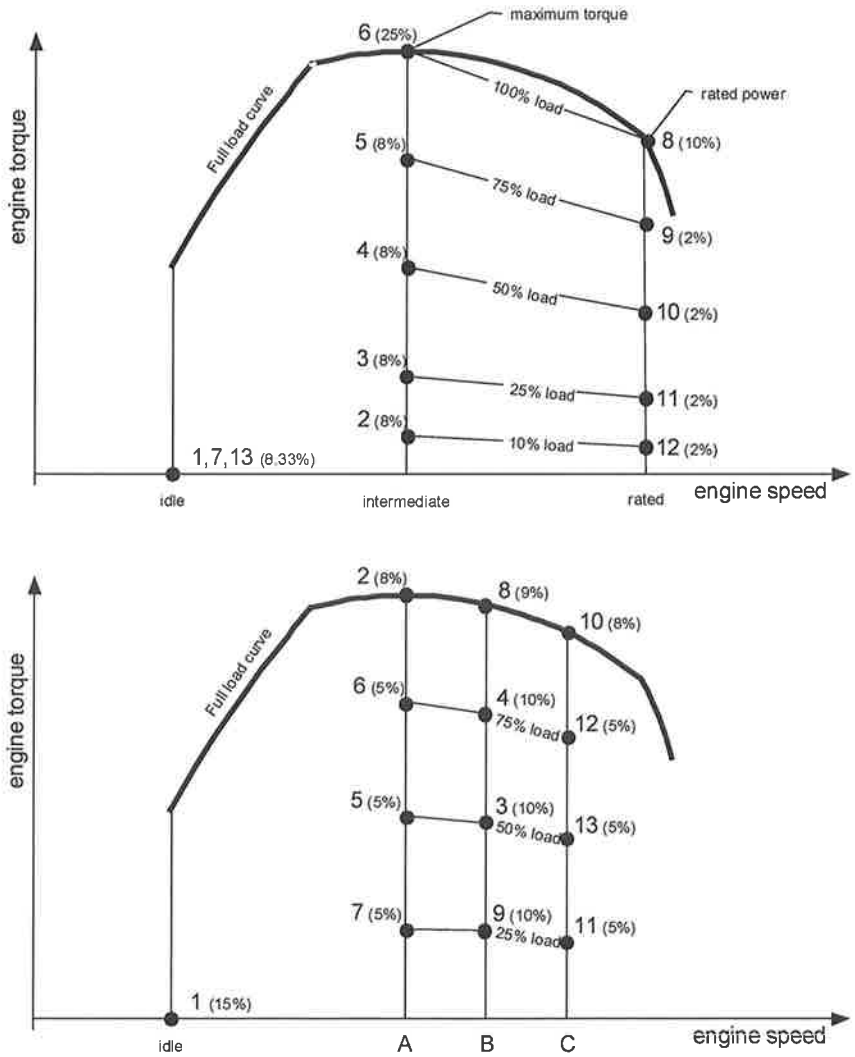


Figure C.1 – Overview of the modepoints for the ECE R49 test (above) and the ESC test (below). Weighting factors are given as a percentage (between brackets)

The type approval certificates for the selected engine types, according to Directives 88/77/EEC, 91/542/EEC and 72/306/EEC and 80/1269/EEC, are requested from the vehicle importers. This information is used to check whether

the engine falls within the type approval specification and to set certain parameters according to those specifications.

The description of the measurement activities below is given for the Euro 2 ECE R49 13-mode test, with the applicable Directive 88/77/EEC. The procedure for Euro 3 vehicles is largely the same, but then the ESC 13-mode test is used, with the applicable Directive 1999/96/EC. An overview of the modepoints in both testcycles is presented in Figure C.1

The measurement programme, outlined in Figure C.2, can be divided in two main steps:

- Preparing for the emission measurements
- Carrying out the measurements

The measurement programme takes approximately 5 working days to complete, and is described below. Each stage of the measurement programme is recorded per vehicle in a test book.

Preparing for the emission measurements

The preparations for the measurements take approximately 2 working days per vehicle to complete and consist of the following tasks:

- making a test book;
- carrying out the initial inspection;
- instrument the vehicle;
- optimise the weight of the rear axle;
- determine the dynamic wheel radius/inspect transmission ratios
- measuring power/perform lambda check.

Vehicle check

On arrival of the vehicle at TNO, an initial check is carried out using an inspection list. This check determines whether the truck is really suitable for the execution of a representative test and whether the vehicle complies with the specifications. In the initial check the following points are checked:

- Engine type number;
- make and type of speed governor;
- check of EEC approval number;
- truck's registration number;
- truck make and type;
- transmission make and type;
- rear axle make and type;
- make and type of tyres;
- presence of injection pump seal;
- injection timing;
- leak-proof exhaust system;
- wheel pressure driven axle;
- level of engine-oil and coolant
- tyre pressure.

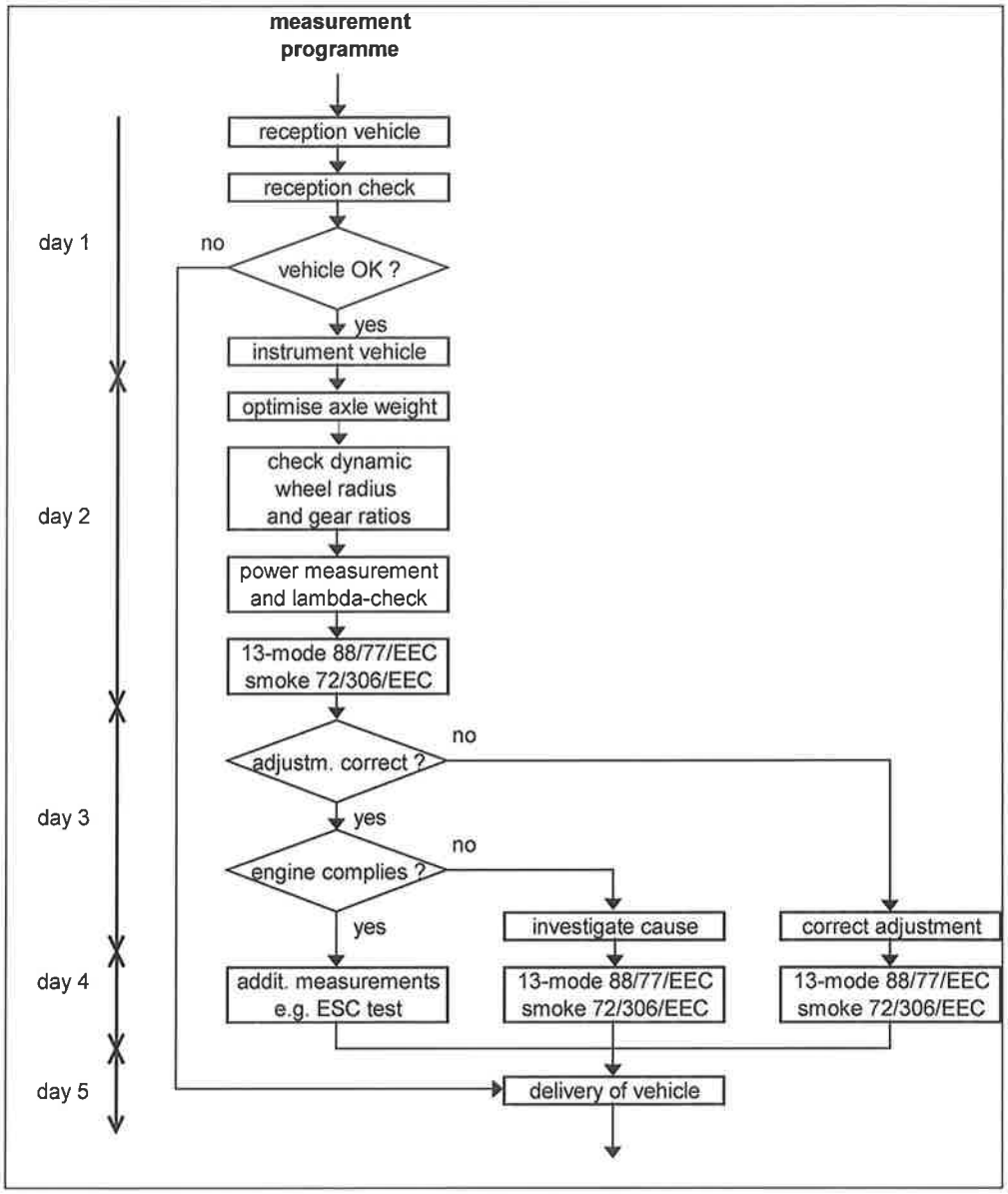


Figure C.2 - Measurement programme for Euro 2 vehicles

Instrumentation of the vehicle

For calculation of the final result of a 13-mode test, at least the following quantities have to be measured:

- engine speed;
- brake force of the chassis dynamometer;
- roller speed;
- concentration of HC, CO, CO_2, NO_x and O_2-emissions in the exhaust gases;
- air rate: the air rate is determined by means of a laminar flow element. The following quantities are measured for this:
  - pressure drop over the laminar flow element;
  - absolute air pressure in front of the laminar flow element;
  - temperature of inlet air.
- fuel consumption (mass flow);
- atmospheric humidity; this is measured at the position of the laminar flow element;
- fan speed; if the cooling fan of the engine cannot be blocked.

To carry out a 13-mode test in accordance with Directive 88/77/EEC, several more quantities have to be measured:

- exhaust gas back pressure; to measure this, a connector is fixed in the vehicle's exhaust system, to which a pressure sensor is attached;
- inlet depression; this is calculated from the sum of the pressure drop over the air filter of the laminar flow element and the pressure drop over the laminar flow element itself;
- fuel temperature; this is measured by means of a thermocouple on the inlet end of the injection pump;
- oil temperature; through the oil dipstick a thermocouple is placed in the (engine) oil sump;
- coolant temperature; if fitting a thermocouple in the coolant circuit leads to little or no coolant loss during the emission test;
- exhaust gas temperature; this is measured in the exhaust gas measurement system.

In addition to the quantities mentioned above, the temperature and pressure of the inlet air and the temperature of the tyres are also measured. The first two quantities mentioned give an indication of any leaks in the inlet system, the operation of the charge pressure control, etc. These parameters also provide additional information in the event of vehicle breakdowns or if the emission values are exceeded. When instrumenting the vehicle, the inlet air of the brake system air compressor must be prevented from being measured along with the air consumption of the engine. In practice, this amounts to disconnecting the air-compressor inlet tube from the inlet system of the engine. An air filter is attached to the inlet end of the compressor, while the hole in the inlet system of the engine is plugged. All equipment connected for instrumentation purposes is recorded in the test book.

During the initial inspection of the vehicle, the type number of the vehicle, the make and type of the turbocharger, the injection pump and the speed governor and the EEC-approval number are checked to see whether they match the specifications. Deviations of one (or more) of these five points from the specifications can lead to exclusion of the vehicle from the programme. In case of doubt, the importer/manufacturer is contacted.

Carrying out the emission measurements
Before the 13-mode test can be carried out, the filters for the particulate emission must be prepared and the analysers must be calibrated for the correct ranges. The vehicle is warmed up by driving first at partial load and then at full load, during which first the exhaust gas back pressure and then the split-ratio of the dilution tunnel are adjusted. When both have been properly adjusted and the engine temperature is stable, the 13-mode test can be started.

The driver sets the correct speed and the corresponding brake force in each mode. In accordance with the directive, the adjustment of the load point must take place within the first minute of the mode. After the correct setting has been reached, the engine is run in the test point for at least 5 minutes (Euro 3 ESC test: 2 minutes). The determination of the particulate emission (cumulatively measured by means of a Cussons dilution tunnel) occurs as late as possible within these 5 minutes. After the 5 minutes have passed and the assessment of the particulate emission is complete, the test moves on to the next mode-point.

After mode 13 has been measured, the vehicle is stopped. The final results of the emission test are then calculated from the values stored in the data-acquisition system.

The average value during the last minute in a particular mode is calculated per mode and per measured signal. From these individually calculated values, the final result of the 13-mode test is calculated.

In principle, each truck for the IUC programme is tested twice. The first test is carried out with the initial setting. After this test the setting is checked, to find whether it corresponds to the type approval documentation. The following settings are checked:
- injection timing;
- idle speed;
- supply of the injection pump;
- governing of the full-load speed.

If the setting is found to correspond to the type approval documentation and the measured emission values were below the limit values, as a second test an ESC-test is carried out. With the results of this ESC-test it is possible to check the correlation between both tests for conventional technologies. For Euro 3 vehicles (which are already tested on the ESC) a second ESC, or an alternative test may be performed.
The vehicles that are exclusively tested for the N_2O measurement programme are tested only once, except if they have an after-treatment system. In that case the emissions are measured before and after this system.

If the initial setting deviated from the type approval documentation, it was corrected. To do this the following tolerances were adhered to:
- injection timing — as stated in type-approval documentation;
- idle speed — type approval value ± 50 rpm;
- supply injection pump — type approval value ± 5 %;
- governing of the full-load speed — type approval value ± 50 rpm.

Depending on the nature of any discrepancies and the possible consequences for the emission results, correction of the setting is carried out by TNO-Automotive or by the importer/dealer.

After each emission measurement the test data are processed to form a final result, and the vehicle is returned to its owner.

N_2O analyser specifications
The analyser used for the N_2O measurements has the following specifications:

Make	Thermo Instruments
Model	46 C
Preset ranges	0 –10, 20, 50, 100, 200, 500 and 1000 ppm
Custom ranges	0-10 to 1000 ppm
Zero noise	0.15 ppm RMS (30 second time setting)
Lower detectable limit	0.3 ppm
Zero drift (24 hour)	1 ppm
Span drift (24 hour)	+/- 1 % fullscale
Response time	T90 with modification (without capillary) by sampleflow 4.7 l/min ca 13 sec (5 sec time setting) at flow 2.1 l/min ca 22 sec
Linearity	+/- 2 % fullscale

Cross sensitivity	79.9 % CO2 causes an N_2O response off 2 ppm, According to the supplier a concentration of ca 10% CO2 could cause a N2O reading off ~ 1 ppm. The CO_2 is measured as N_2O by the analyser, so the real N_2O-emission is *lower* than indicated by the measurement signal CO has a negative effect on the N_2O reading; the effect is very small therefore it is not taken in account

References

[1] Van Gompel, P. and R. Verbeek, Final report DCM; Procedure and accuracy of testing, according to 88/77/EEC and 72/306/EEC, carried out on a chassis dynamometer, TNO-report 93.OR.VM.023.1/PvG/RV, Delft, 1993

D Measurement results

Euro 1 vehicles

Within the period of the investigation 3 vehicles falling under the Euro 1 prescriptions were tested that were additionally screened on N_2O-emissions. Apart from the N_2O all relevant parameters and regulated emissions have been measured, so as to obtain an impression of the state of the vehicle.
The following vehicles which fall within the Euro 1 specification have been tested (all without catalyst):

- Mercedes 114 ecoliner
- DAF 75.270
- Scania 113.380

It appeared that these vehicles showed hardly any measurable N_2O-emission. For some vehicles the influence of a cold engine on the N_2O-emissions has been additionally monitored. These lay at approximately the same level as those in the 'warm' 13-mode test. In all cases the engine adjustment complied with the relevant manufacturer's specifications. There are no further particular details concerning these vehicles that need mentioning.

As an example the N_2O-emission of the Scania 113.380 is presented in Figure D.1, measured over the complete ECE 49 13-mode testcycle. The individual 13-mode points have been indicated as well; the upper (light coloured) trace shows the engine power of the modes (with a stepwise pattern), whereas the lower (dark coloured) trace shows the N_2O-emission related to a second scale at the right-hand side of the figure. The indication 'I25' does e.g. stand for the 'intermediate' engine speed at 25 % load, 'R50' stands for 'rated' engine speed at 50 % load and 'Idle' is the unloaded idle speed.

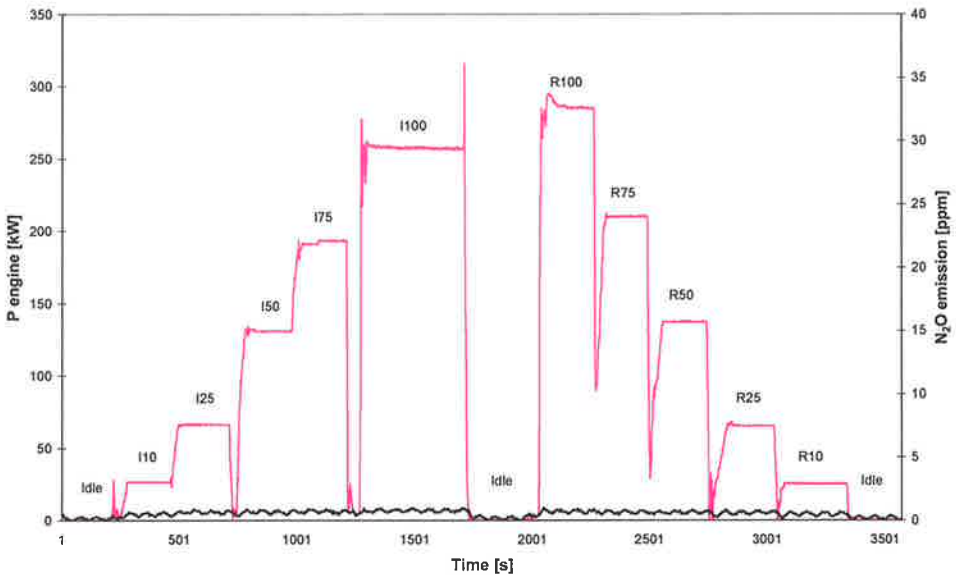


Figure D.1 – Online N_2O-emission of the Scania 113.380 with Euro 1 engine over the ECE R49 13-mode testcycle

Euro 3 vehicles

This programme to screen N_2O-emissions from HD vehicles was connected to the project *In-use compliance programme for trucks*, so that HD vehicles from the Dutch fleet could be measured on a chassis dynamometer in an ESC 13-mode test. Since the start of the investigation 29 Euro 3 vehicles within this in-use compliance programme have been measured, on which an additional screening of the N_2O-emission was performed. One engine type (three vehicles tested) is equipped with an EGR system; all other vehicles did not have any kind of exhaust after-treatment device installed. The following 29 vehicles which fall within the Euro 3 specification have been measured:

Manufacturer	Vehicle type	Vehicles tested
DAF	XF380	3
DAF	CF220	1
DAF	65.220	2
DAF	75.250	4
IVECO	Stralis 400	2
MAN	TG-A 410 (with EGR)	3
MERCEDES	Atego 8.15	2
MERCEDES	Atego 12.18L	1
RENAULT	Premium DCi 420	3
SCANIA	114.340	3
VOLVO	FL6.220	2
VOLVO	FH12.420	3
Total		**29**

It appeared that all of these vehicles showed hardly any measurable N_2O-emission. In the case of some of these vehicles an additional check was made of the N_2O-emissions after a cold start. These were of the same order as those in the hot test. Most engines proved to be in good condition because they were in accordance with the manufacturer specifications, and fulfilled the applicable type approval limits. Only one engine type (three vehicles with this engine were tested) encountered some problems to comply with the Euro 3 emission standards. This problem was resolved, and will most likely not have affected the N_2O-emission. There are no further particular details concerning these vehicles that need mentioning.

As a typical example for the Euro 3 vehicles, Figure D.2 shows the on-line N_2O-emission measured over the complete 13-mode testcycle. In this figure the 13-mode points are shown as well: the upper (light coloured) trace shows the engine power of the modes (with a stepwise pattern), whereas the lower (dark coloured) trace shows the N_2O-emission related to a second scale at the right-hand side of the figure. As to the legends given: 'B75' does e.g. mean the 'B' engine speed at 75 % load.

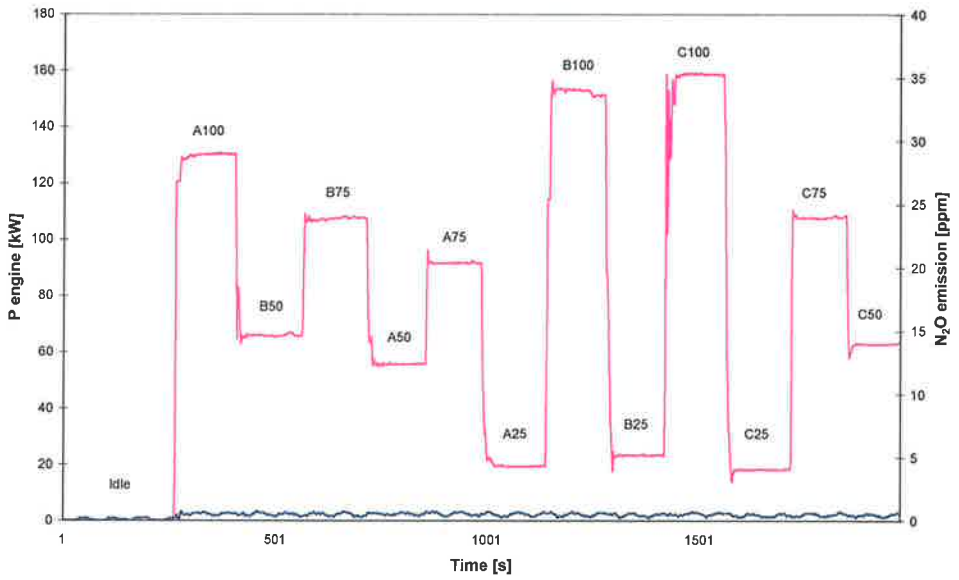


Figure D.2 - Typical online N_2O-emission for Euro 3 vehicles over the ESC 13-mode testcycle.

Euro 2 urban buses with CRT filter

Five city buses were tested that were fitted with a continuously regenerating particulate trap (CRT). The first three vehicles were DAF/Berkhof of the type SB220 with a GS160M Euro 2 engine, fitted with an Eminox continuously regenerating particulate trap type 'CO 31756'. The fourth and fifth buses were both manufactured by Mercedes (type O0408), with a OM447hLA II/1 Euro 2 engine, fitted with an Eminox continuously regenerating particulate trap type 'CO 31756'.

First vehicle – DAF/Berkhof
The first bus showed a very low N_2O-emission of 2 ppm on average, and a peak value of 9 ppm. Weighted over the testcycle this amounts to 0.02 g/kWh.

During the test the temperature of the trap increased higher than is usual during operation in the field, causing the start of a rather sudden regeneration of a relatively large amount of filtered soot. This happened notwithstanding the fact that preceding the actual test the trap had been slowly heated on the chassis dynamometer, so as to give the collected soot the chance to burn off. The temperature rise of this combustion (an exothermic reaction) did damage the trap to such an extent that it had to be replaced. For that reason the measured particulate emission over this test could not be regarded as representative for a vehicle fitted with a CRT filter. The other measurement results, such as fuel consumption, power delivered and regulated emissions did comply with the manufacturer's specifications.

So as to obtain a suitable impression of the emissions of a Euro 2 engine during the cold start phase a cold start measurement was carried out on this bus, where the emissions were measured before the particulate trap. It turned out that the N_2O-emission was nearly zero during the warming-up phase. This result has been used to predict the N_2O-emission factor for Euro 2 engines, since there were no separate measurements foreseen to screen Euro 2 engine technology.

Figure D.3 shows the online N_2O-emission of the first bus, measured over the complete ECE R49 13-mode testcycle. The individual 13-mode points have been indicated as well; the upper (light coloured) trace shows the engine power of the modes (with a stepwise pattern), whereas the lower (dark coloured) trace shows the N_2O-emission related to a second scale at the right-hand side of the figure. The indication 'I25' does e.g. stand for the 'intermediate' engine speed at 25 % load, 'R50' stands for 'rated' engine speed at 50 % load and 'Idle' is the unloaded idle speed.

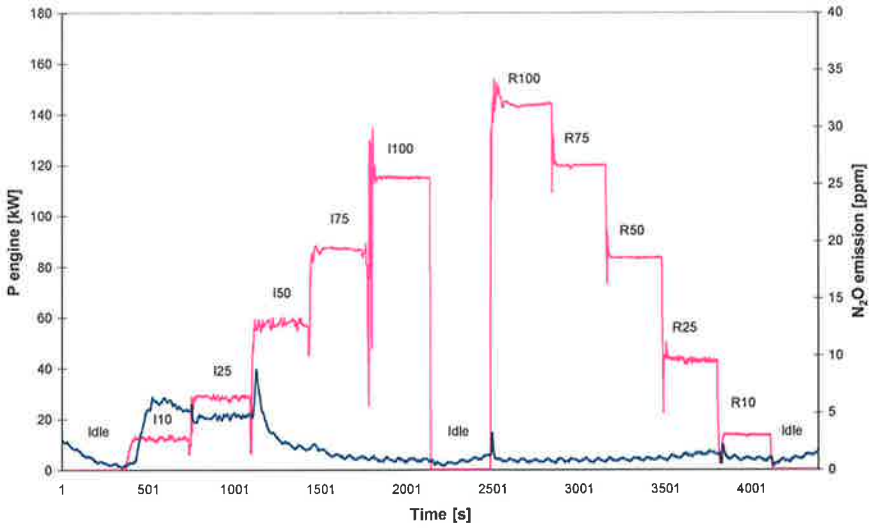


Figure D.3 - The online N2O-emission of the first bus with particulate trap over the ECE R49 13-mode testcycle.

Second vehicle - DAF/Berkhof
The particulate trap of this bus had already been serviced by the manufacturer shortly before the testing. 'Servicing' means; dismounting of the filter element, checking the condition of the filter and reassembly of the unit. The intention is that the exhaust flow 'blows' the filter clean. Notwithstanding a careful warming up of the trap on the chassis dynamometer in preparation for the test, the filter was still damaged. In consultation with the manufacturer a new one was mounted in order to be able to carry on with the testing.

The bus emitted only 1.5 ppm on average over the testcycle, with a peak value of 7 ppm. Weighted over the testcycle this amounts to 0.01 g/kWh. A measurement of the N_2O-emission before the trap showed that the engine itself hardly emitted any detectable N_2O. This result has been used to predict the N_2O-emission factor for Euro 2 engines, since there were no separate measurements foreseen to screen Euro 2 engine technology.
Additionally, cold start measurements were performed on this bus, measured after the trap. On average this bus emitted 1 to 2 ppm N_2O, with one peak value at the start of the warming up phase of approximately 10 ppm.

Figure D.4 shows the online N_2O-emission of the second bus, measured over the complete ECE R49 13-mode testcycle. In this figure the individual 13-mode points have been indicated as well, in an identical way to Figure D.3.

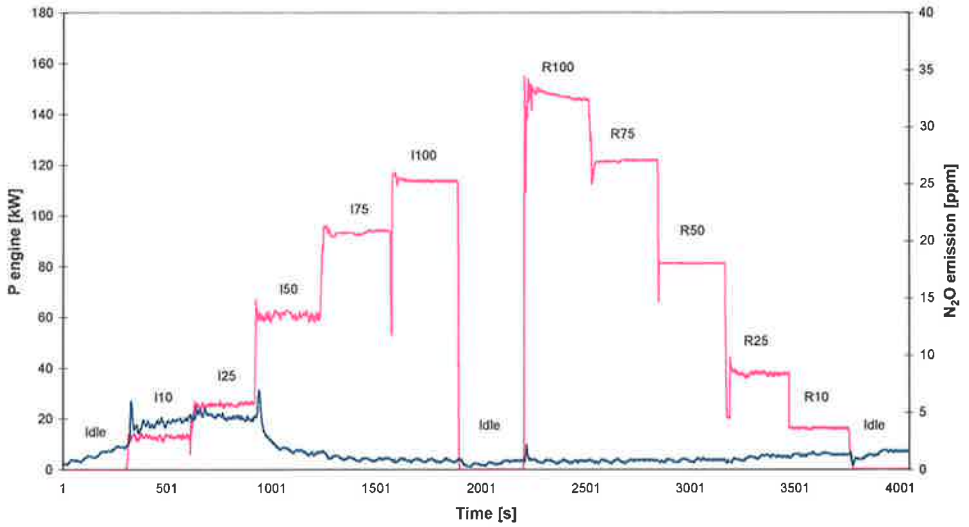


Figure D.4 - Online N_2O-emission of the second bus with particulate trap over the ECE R49 13-mode testcycle.

Third vehicle - DAF/Berkhof

The third bus showed a low N_2O-emission of on average 2 ppm, and a peak value of 12 ppm. Weighted over the testcycle this amounts to 0.02 g/kWh. Additionally measurements with a cold engine were performed on this bus, again measured after the trap. On average this bus emitted 1 to 2 ppm N_2O, with one peak value at the start of the warming up phase of approximately 12 ppm. Before the test the trap had been prepared by the manufacturer. The fuel consumption, engine power and regulated emissions (with the exception of the particulates) of this vehicle complied with the manufacturer's specifications.

Figure D.5 shows the online N_2O-emission of the third bus, measured over the complete ECE R49 13-mode testcycle. In this figure the individual 13-mode points have been indicated as well, in an identical way to Figure D.3.

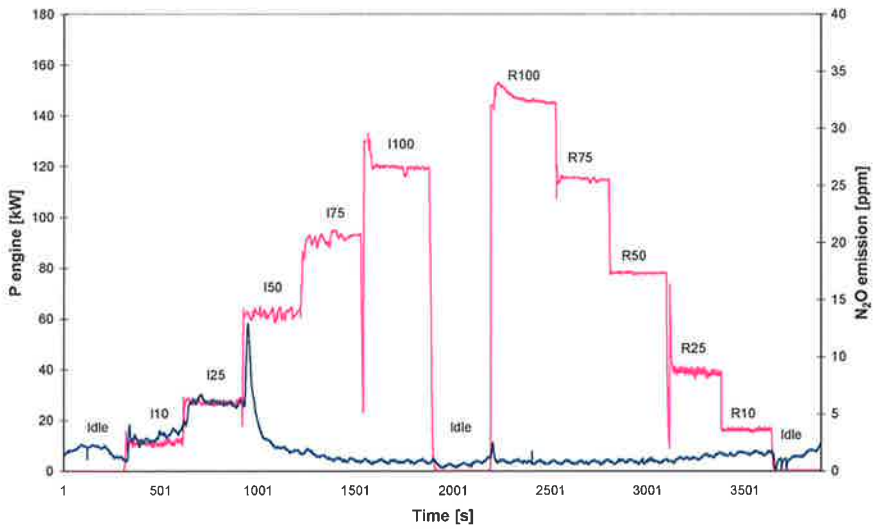


Figure D.5 - Online N_2O-emission of the third bus with particulate trap over the ECE R49 13-mode testcycle.

The N_2O-emissions have also been measured upstream of the CRT filter. It appeared that hardly any N_2O is emitted by the engine itself. This result has been used to predict the N_2O-emission factor for Euro 2 engines, since there were no separate measurements foreseen to screen Euro 2 engine technology.

Fourth vehicle - Mercedes
This bus engine emitted only 1 ppm on average over the testcycle, with a peak value of only 4 ppm. Weighted over the testcycle this amounts to 0.01 g/kWh. A measurement of the N_2O-emission before the trap showed that the engine itself hardly emitted any detectable N_2O. This result has been used to predict the N_2O-emission factor for Euro 2 engines, since there were no separate measurements foreseen to screen Euro 2 engine technology.
Additionally, measurements with a cold engine were performed on this bus, measured after the trap. On average this bus emitted 1 to 2 ppm N_2O, with one peak value at the start of the warming up phase of approximately 5 ppm.

Figure D.6 shows the online N_2O-emission of the fourth bus, measured over the complete ECE R49 13-mode testcycle. In this figure the individual 13-mode points have been indicated as well, in an identical way to Figure D.3.

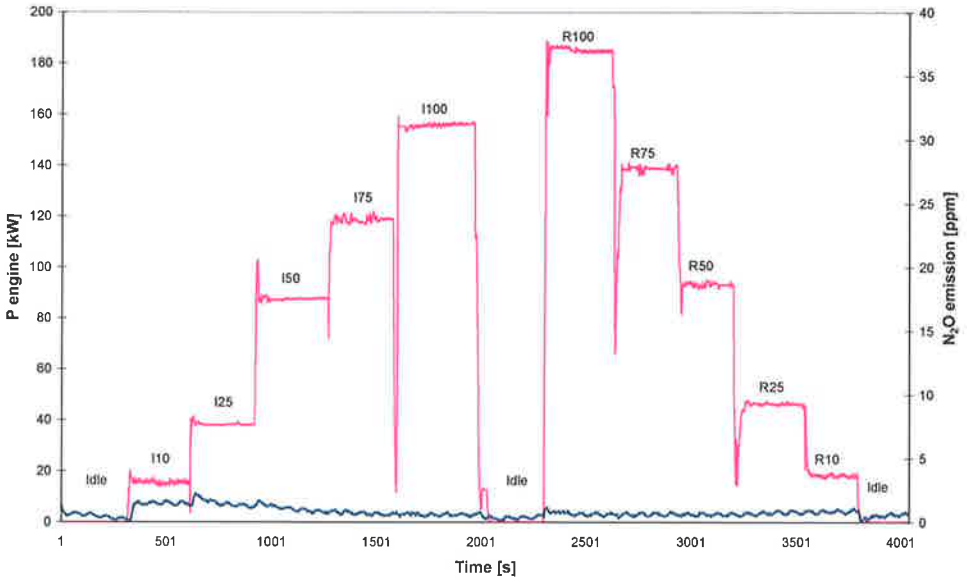


Figure D.6 - Online N_2O-emission of the fourth bus with particulate trap over the ECE R49 13-mode testcycle.

Fifth vehicle - Mercedes
The fifth bus showed more or less the same picture as the fourth bus. The engine emitted approximately 5 ppm on average over the testcycle, with a peak value of 5 ppm. Weighted over the testcycle this amounts to 0.01 g/kWh. A measurement of the N_2O-emission before the trap showed that the engine itself hardly emitted any detectable N_2O. This result has been used to predict the N_2O-emission factor for Euro 2 engines, since there were no separate measurements foreseen to screen Euro 2 engine technology.
Additionally measurements with a cold engine were performed on this bus, measured after the trap. On average this bus emitted 1 to 2 ppm N_2O, with one peak value at the start of the warming up phase of approximately 5 ppm.

Figure D.7 shows the online N_2O-emission of the fifth bus, measured over the complete ECE R49 13-mode testcycle. In this figure the individual 13-mode points have been indicated as well, in an identical way to Figure D.3.

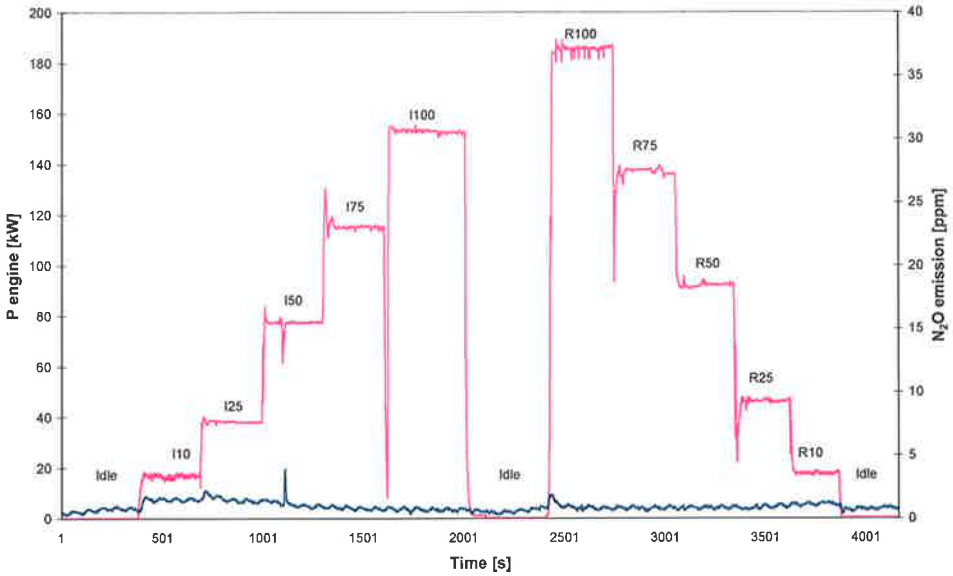


Figure D.7 - Online N_2O-emission of the fifth bus with particulate trap over the ECE R49 13-mode testcycle.

Overall result for Euro 2 engines with CRT filter
In summary it can be said that the pattern of the N_2O-emission over the 13-mode test turned out to be reasonably reproducible for the 5 tested vehicles, and that the DAF engines produced relatively higher and the Mercedes engines relatively lower emissions. Noteworthy is that the N_2O-emission shows an increasing trend with increasing power over the first three to four load points, after which it rapidly decreases to a low value, almost independent of the power. It seems that this emission only occurs within a narrow (and relatively low) temperature window.

Demonstrator vehicles – SCRdeNOx after-treatment

Two demonstration vehicles were tested with a SCRdeNOx catalyst as after-treatment. Of the first one it had already been decided at the start of the project to measure it. The other vehicle happened to be present at TNO and could be added to the investigation as an additional test object. For both vehicles the NH_3-emissions were screened as well. The vehicles complied with the manufacturer's specifications. For reasons of confidentiality the manufacturer and the type indication are omitted here.

First vehicle
This vehicle emitted 2.5 ppm N_2O on average over the testcycle, with a peak value of 20 ppm. Weighted over the testcycle this is equivalent to 0.03 g/kWh. There was no cold start measurement performed on this vehicle.

Figure D.8 shows the on-line N_2O-emission of the vehicle concerned, measured over the complete 13-mode testcycle. In this figure the 13-mode points are shown as well: the upper (light coloured) trace shows the engine power of the modes (with a stepwise pattern), whereas the lower (dark coloured) trace shows the N_2O-emission related to a

second scale at the right-hand side of the figure. As to the legends given: 'B75' does e.g. mean the 'B' engine speed at 75 % load.

From this figure it can be concluded that:

- the N_2O-emission shows a tendency to increase during each load condition ('mode point'), probably as a result of an increasing temperature in the catalyst;
- the N_2O-emission reaches its maximum value at the end of each load condition, but does not yet seem to have stabilised at all at that point;
- the N_2O-emission shows a bigger increase for the highest load points (75 % and 100 %);
- the N_2O-emission is higher at the lower engine test speeds (especially speed 'A').

The N_2O-emission before the catalyst was hardly above the minimum detection level (in the order of 1 to 2 ppm).

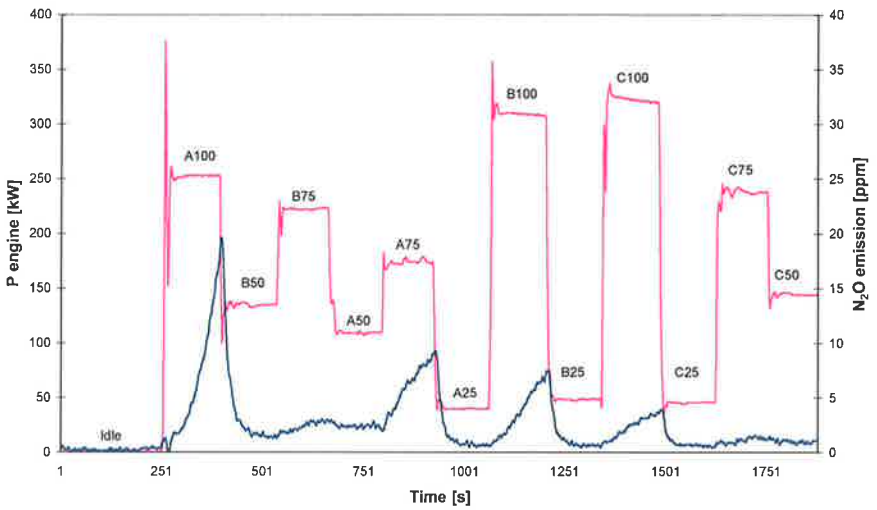


Figure D.8 - Online N_2O-emission of SCRdeNOx vehicle 1 over the ESC 13-mode testcycle.

Since during the testing an additional NH_3-analyser was available, the ammonia slip of the SCRdeNOx system was also monitored. This is shown in Figure D.9.

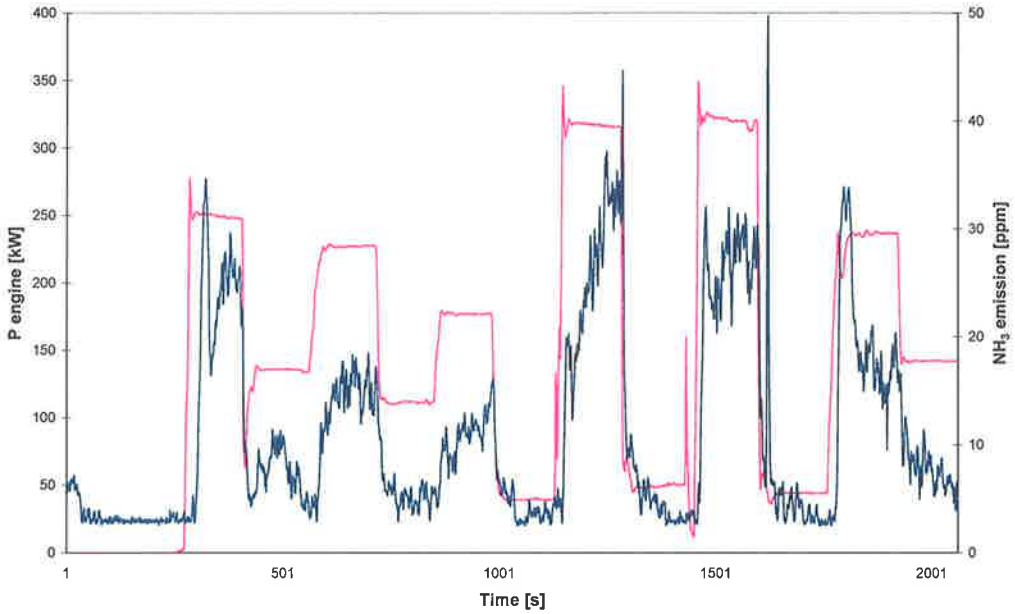


Figure D.9 - Online NH_3-emission of SCRdeNOx vehicle 1 over the ESC 13-mode testcycle.

The NH_3-emission is somewhat higher than the N_2O-emission level, but as such is still quite low. It must be noted that there was no NH_3 clean-up catalyst installed.

Second vehicle
Vehicle 2 emitted on average 6 ppm N_2O with a peak value of 30 ppm. Weighted over the testcycle this is equivalent to 0.07 g/kWh.

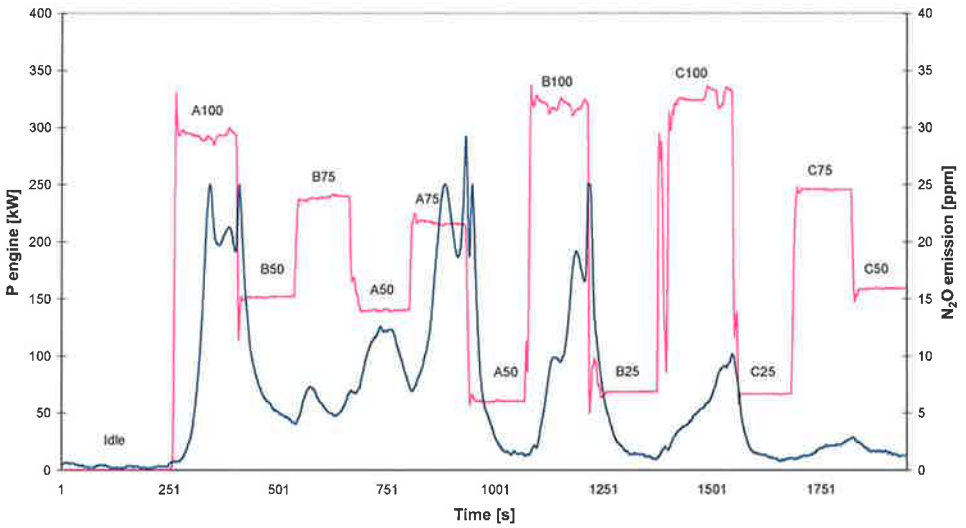


Figure D.10 - Online N_2O-emission of SCRdeNOx vehicle 2 over the ESC 13-mode testcycle.

Figure D.10 shows the online N_2O-emission of this vehicle, measured over the complete 13-mode testcycle. The same remarks as made for the first vehicle seem to apply here also, although the N_2O-emission does seem to stabilise somewhat more at certain load points (see 'A100' and 'A75'). Additionally, a cold start measurement was

made on this vehicle, but this resulted in a much lower result; the average N_2O-emission was 1 to 2 ppm with a peak value below 3 ppm.

The N_2O-emission before the catalyst was hardly detectable (in the order of 1 to 2 ppm).

Since during the testing an additional NH_3-analyser was available, the ammonia slip of the SCRdeNOx system was also monitored. This is shown in Figure D.11.

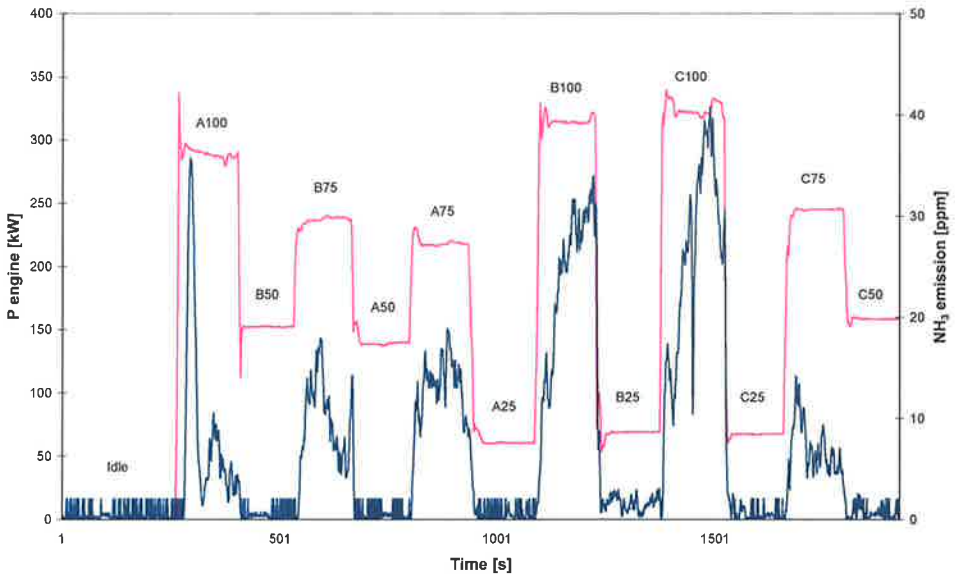


Figure D.11 - Online NH_3-emission of SCRdeNOx vehicle 2 over the ESC 13-mode testcycle.

Also for this vehicle there is little ammonia slip, but the NH_3 -emission is somewhat higher than the emission of N_2O. It must be noted that there is no NH_3 clean-up catalyst installed.

Demonstrator vehicles – EGR plus particulate filter after-treatment

One of the demonstration vehicles tested was fitted with EGR and a DPF (diesel particulate filter) of the CRT type. For reasons of confidentiality the manufacturer and type indication have been omitted here. On this vehicle no significant amount of N_2O was detected, either before or after the filter. The fuel consumption, engine power and regulated emissions of this vehicle complied with the manufacturer's specifications. An additional cold start measurement was performed, but this did not show a different picture as far as N_2O-emissions were concerned. Figure D.12 shows the online N_2O-emission, measured over the complete ESC 13-mode testcycle.

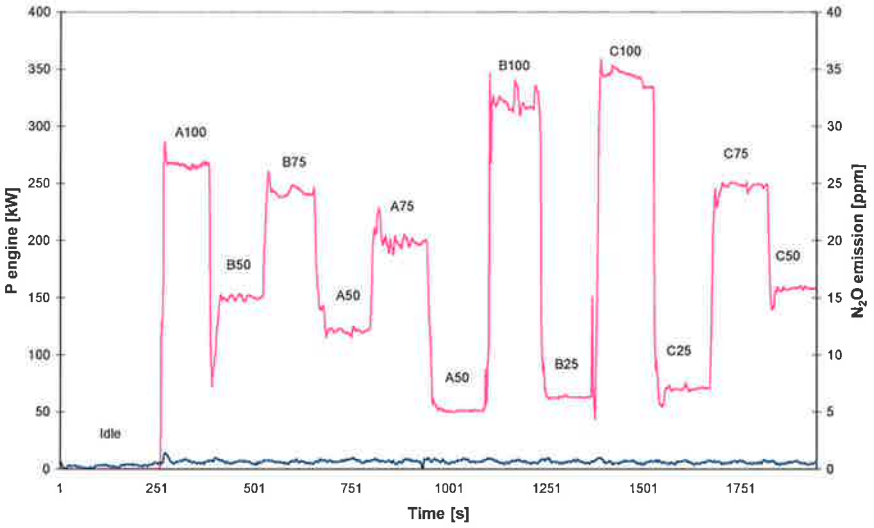


Figure D.12 - Online N_2O-emission of the demonstrator vehicle with EGR and CRT over the ESC 13-mode testcycle.

CNG vehicles

Two vehicles have been tested, with different CNG technologies. The first vehicle was a refuse collection vehicle of Volvo, with a lean-burn Euro 2 engine and an oxidation catalyst. The second vehicle was a Euro 2 MAN refuse collection vehicle, with a stoichiometric lambda-controlled engine and three-way catalyst.

First vehicle

The engine appeared to be in good condition, though the NO_x-emission was at a rather high level. By consulting the maintenance shop it was found out that an alternative EPROM was used in the engine control system. This enables a somewhat richer mixture, resulting in higher engine power and torque and -as a consequence- more NO_x-emission. Despite the higher NO_x, the N_2O-emission was hardly measurable: 0.6 ppm on average, and a highest peak of 7.5 ppm. Weighted over the test cycle this amounts to only 0.005 g/kWh. The richer mixture also appears from the high HC-emissions. The methane share of the HC-emission was 94%.

Figure D.13 shows the online N_2O-emission of this vehicle, measured over the complete ECE R49 13-mode testcycle. In this figure the individual 13-mode points have been indicated as well, in an identical way to Figure D.1.

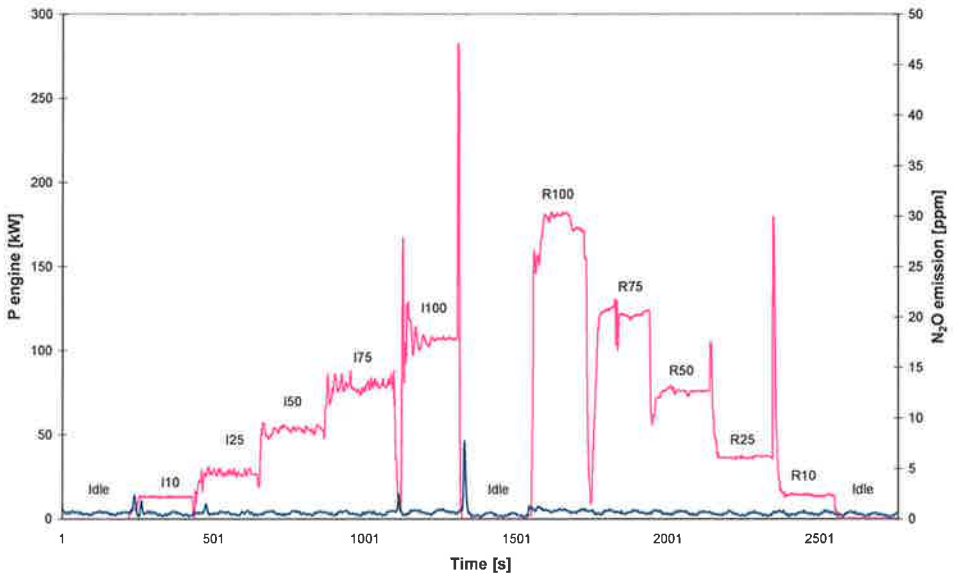


Figure D.13 - Online N_2O-emission of the first CNG vehicle with lean-burn engine and oxidation catalyst over the ECE R49 13-mode testcycle.

Second vehicle

Over the 13-mode test the control system did not seem to be able to keep the lambda at '1'. In a stoichiometric engine with a three-way catalyst, even small deviations from the lambda = 1 setting (so-called 'lambda excursions') immediately result in higher NO_x-emissions (lambda > 1) or higher CO and HC-emissions (lambda < 1). In this case, the leaner mixture clearly caused high NO_x-emissions, and consequently also N_2O-emissions. At the same time, HC-emissions were rather low (94% of this emission consists of methane). On average the N_2O-emission amounted to 5 ppm, with a highest peak of 23 ppm. When the official ECE R49 weighting factors are applied (taking the average N_2O-emission level over the last 30 seconds of the modepoints), the overall N_2O-emission result is 0.06 g/kWh.

Because of the high NO_x-emission, the measured N_2O-emission could not be considered to be representative for this kind of CNG technology. The manufacturer of the vehicle was consulted in order to find the reason for the unusual emission behaviour. After a thorough inspection and adjustments made to the fuel system, it was found out that the EPROM used in the ECU is not suitable for the CNG quality used in the Netherlands. A second test was performed, after the correct EPROM was installed. The NO_x-emission now decreased to a comparable level of the type approval value, and as a consequence also the N_2O-emission dropped to 0.02 g/kWh over the 13-mode test (on average 3 ppm, with a highest peak of 8 ppm).

Figure D.14 shows the online N_2O-emission of this vehicle, measured over the complete ECE R49 13-mode testcycle. In this figure the individual 13-mode points have been indicated as well, in an identical way to Figure D.1. The dark blue and green line respectively represent the N_2O signal for the first and second test.

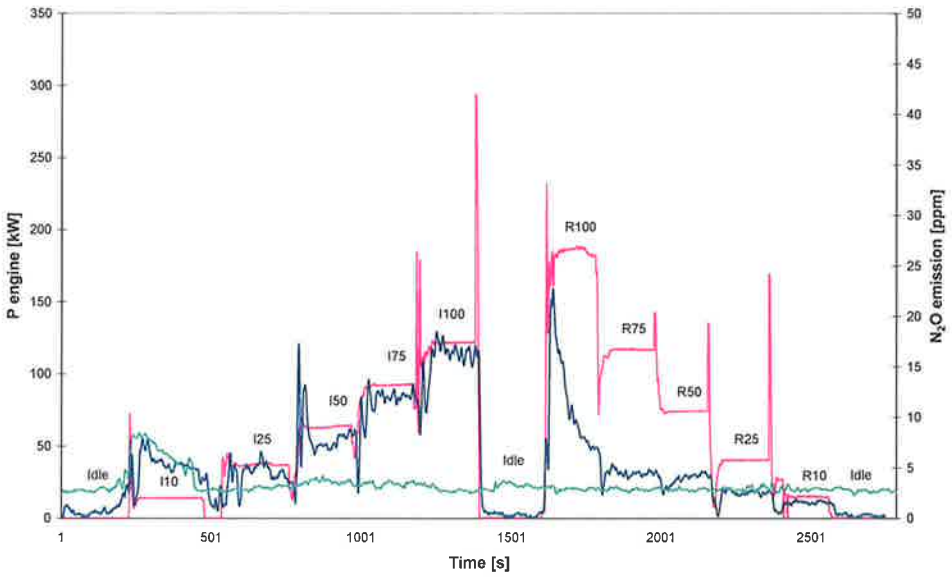


Figure D.14 - Online N_2O-emission of the second CNG vehicle with stoichiometric engine and three-way catalyst over the ECE R49 13-mode testcycle (1st test).

The N_2O-emission behaviour in the second test is rather strange, since it stays constant at 3 ppm after the 'I10' modepoint has been tested. Though the N_2O-analyser is calibrated before each test, it seems that the 'zero signal' has been shifted some 3 ppm upwards. This is plausible, as 'I10' is the only modepoint where NO_x-emissions (a prerequisite for N_2O formation) are clearly present. With hardly any NO_x-emissions produced over the other modepoints, a nearly zero N_2O-emission would be expected. Because of this result, it is difficult to predict a representative N_2O-emission level for this type of engine technology, especially since only engine has been tested. However, it is most likely to be lower than the measured 0.02 g/kWh.

After the first test, the vehicle was also tested with a cold start (not a full 13-mode test). Both NO_x- and N_2O-emissions were at a considerable lower level than in the hot test. Apparently, during the cold test the engine remained a shorter period in the temperature window favourable for N_2O formation.

E Assumptions for calculation of national N_2O-emission

In Paragraph 5.3 a rough estimation has been calculated for the national N_2O-emissions. As indicated, several assumptions had to be made in order to come up with a result. In order to provide insight into the background of this calculation, the method and the assumptions are presented in this Appendix. It would stretch too far to give a full motivation for each of the assumptions made, so they are described without further details.

The calculation has mainly been based on the following sources of information:

- Statline – online statistics from the CBS website (www.cbs.nl)
- Brink, R.M.M. van der, *Verkeer en Vervoer in de Milieubalans 2000*, RIVM rapport 251701044, December 2000, Bilthoven
- Internal information sources and expert guesses

The method for the calculation consists of the following steps:

1. The emissions in mg/km are weighed according to the share of kilometres driven on urban roads, rural roads and highways. For HD vehicles, this share is on average assumed at 23%, 24% and 53% respectively. For Euro 4 and 5, two different scenario's are worked out: Scenario 1 contains only vehicles with SCRdeNOx systems; Scenario 2 is a mix of 80% vehicles with SCRdeNOx and 20% with EGR and CRT. This results in the following emission factors for the subsequent Euro classes:

Euro 1 vehicles	
Light truck	4.2
Medium truck	8.3
Heavy truck	12.7
Heavy truck	13.8
Truck with trailer/semitrailer	13.7
Truck with trailer/semitrailer	14.8
City bus	9.3

Truck with SCRdeNOx (Euro 4 and 5)	
Light truck	20.9
Medium truck	41.8
Heavy truck	63.9
Heavy truck	79.3
Truck with trailer/semitrailer	68.8
Truck with trailer/semitrailer	85.4
City bus	46.7

Euro 2 vehicles	
Light truck	4.0
Medium truck	8.0
Heavy truck	12.2
Heavy truck	13.4
Truck with trailer/semitrailer	13.2
Truck with trailer/semitrailer	14.4
City bus	8.9

Truck with EGR & CRT (Euro 4 and 5)	
Light truck	2.3
Medium truck	4.6
Heavy truck	7.1
Heavy truck	7.8
Truck with trailer/semitrailer	7.6
Truck with trailer/semitrailer	8.4
City bus	5.2

Euro 3 vehicles	
Light truck	2.4
Medium truck	4.8
Heavy truck	7.3
Heavy truck	8.2
Truck with trailer/semitrailer	7.9
Truck with trailer/semitrailer	8.8
City bus	5.4

Emissions in mg/km for different vehicle- and Euro classes, weighed according to the distance covered on urban roads, rural roads and highways

2. The next step is to determine the fleet composition. For the 'Heavy truck' and 'Truck with trailer/semitrailer' vehicle types the half loaded categories are used, assuming that on average those vehicles will be about half loaded. The (estimated) fleet composition is based on vehicle ownership. For the calculation of emission, this fleet has to be weighed according to the annual distance covered by each vehicle class; this provides the actual fleet composition on the road. The assumed annual kilometres driven by an average HD vehicle 50,448 km.

Vehicle category	GVW [tonne]	Load [tonne]	Actual weight [tonne]	Fleet composition [%]	Annual distance [km]	Weighed fleet composition [%]
Light truck	6.8	fully loaded	6.8	30	40927	26
Medium truck	13.6	fully loaded	13.6	17	40927	15
Heavy truck	37.1	half loaded	20.8	13	40927	11
Truck with trailer/semitrailer	40	half loaded	22.4	36	55509	43
City bus	15.2	fully loaded	15.2	4	54909	5

Vehicle classes used for the calculation; the weighed fleet composition takes the annual driven distance into account (relative to the average annual distance)

3. The third component to finalise the emission calculation is the total number of vehicles in the Netherlands, and the annual sales numbers. From the available data, the status in 1999 was used as a reference, and the annual growth in sales was determined at a constant 2.5% between 1988 and 2010. For the years in which a shift to a higher Euro class took place, the sales number is assumed to be equally distributed amongst the two classes. The vehicles that have disappeared from the Dutch roads are assumed to be of the eldest present Euro class. The national N_2O emissions follow from multiplying the vectors for number of vehicles per vehicle class, with the (distance) weighed emission factors per Euro class and the average annual driven kilometres (and a factor of 10^{-12} to convert mg into ktons).

Year	Total number	Sales number	(pre) Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	N_2O emission [kton] - 1	N_2O emission [kton] - 2
1988	139751	12628	139751					0.07	0.07
1989	143335	12952	143335					0.07	0.07
1990	147010	13284	147010					0.07	0.07
1991	150779	13625	150779					0.08	0.08
1992	154646	13974	154646					0.08	0.08
1993	158611	14332	158611					0.08	0.08
1994	162678	14700	162678					0.08	0.08
1995	166849	15077	166849					0.08	0.08
1996	171127	15463	171127					0.09	0.09
1997	175515	15860	159655	15860				0.09	0.09
1998	180016	16266	147889	32126				0.09	0.09
1999	184631	16683	135822	48810				0.09	0.09
2000	189365	17111	123445	65921				0.09	0.09
2001	194221	17550	110750	74696	8775			0.10	0.10
2002	199201	18000	97730	74696	26775			0.09	0.09
2003	204181	18450	84260	74696	45225			0.09	0.09
2004	209286	18911	70453	74696	64136			0.09	0.09
2005	214518	19384	56302	74696	83520			0.09	0.09
2006	219881	19869	51730	74696	93455	9934		0.12	0.11
2007	225378	20365	26928	74696	93455	30300		0.15	0.14
2008	231012	20874	11688	74696	93455	51174		0.20	0.18
2009	236787	21396	0	70762	93455	72570		0.25	0.21
2010	242707	21931	0	54751	93455	83536	10966	0.30	0.25

Number of vehicles, sales numbers, shares in Euro classes and the resulting national N_2O-emissions of HD vehicles in the Netherlands for 2 scenario's