

CYCLIC NO₂:NO_x RATIO FROM A DIESEL ENGINE **UNDERGOING TRANSIENT LOAD STEPS**

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Abstract

As the control of real driving emissions continues to increase in importance, the importance of understanding emissions formation mechanisms during engine transients similarly increases. Knowledge of the NO₂/NO_x ratio emitted from a diesel engine is necessary, particularly for ensuring optimum performance of NO_x aftertreatment systems. In this work cycle-to-cycle NO and NO_x emissions have been measured using a Cambustion CLD500, and the cyclic NO₂/NO_x ratio calculated as a high speed light duty diesel engine undergoes transient steps in load while all other engine parameters are held constant across a wide range of operating conditions with and without EGR. The results show that changes in NO and NO_x, and hence NO₂/NO_x ratio, are instantaneous upon a step change in engine load. NO₂/NO_x ratios have been observed in line with previously reported results, although at the lightest engine loads and at high levels of EGR higher levels of NO₂ than have been previously reported in the literature are observed.

Introduction

Reducing tailpipe NO_x emissions from diesel engines at all engine operating points is a key research target for the automotive industry¹. Measures such as EGR to control these emissions at steady state are well established², and reasonable transient control has been achieved with aftertreatment technologies such as LNT and SCR³. Nevertheless, an increased understanding of both NO and NO₂ formation mechanisms in-engine is required for further comprehensive reductions in NO_x both in engine-out terms and with aftertreatment.

Recently, Real Driving Emissions (RDE) have become a driver for improvements in urban air quality. In order to meet RDE requirements, a better understanding of NO_x formation in a wide range of engine

transients, and ideally in each engine cycle is needed. Much of today's instrumentation is not suited to measurements during these transients, typically having a response time of seconds⁴ whereas a typical transient event may last substantially less than a second. Instantaneous responses in NO emissions to changes in engine load have been observed previously on a heavy duty diesel engine by Hagena *et al.*⁵. Likewise, NO and NO₂ formation in-cylinder has been studied using a snatch-sampling valve, showing similar increases in NO and NO₂ formation in response to increases in engine load⁶.

Diesel engine NO_x formation is complex and frequently modelled by the so called extended Zel'dovich mechanisms⁷, which are a thermal formation mechanism and thought to dominate in diesel engines⁶:



Above 1000 K, which is typically experienced in diesel combustion cycles, the NO is quickly converted to NO₂ through the following mechanism⁸:



Above 1500 K (again, typical for most diesel combustion cycles) this NO₂ is converted back to NO by the following mechanism⁶:



However, this reaction can be stopped or avoided through flame quench by cooler fluid, which is possible at light load⁹, as EGR levels are increased, or in low temperature combustion (LTC) modes¹⁰; this results in some NO₂ not being reconverted to NO. It would therefore be expected that conditions where higher levels of NO₂ were observed would be conditions with low overall levels of NO_x as the temperatures are not sufficiently high for high levels of formation. As a result, whereas typical NO₂ levels might usually be 10 % at light load, NO₂ can comprise up to 30 % of total NO_x⁹ and in LTC up to 70 %¹⁰.

While NO_x emissions can be modelled – 1-D simulations of NO_x emissions using the Zel'dovich equations have been undertaken and report accuracies of the order of $\pm 10\%$ ^{11, 12} having been tuned using relevant experimental data. Modelling NO₂ levels as part of total NO_x in CFD usually results in high levels of simulation tuning – often using fixed NO : NO₂ ratios obtained from experiments^{13, 14}.

The effect that a number of diesel engine parameters has on the NO_2/NO_x ratio has been investigated in comprehensive work by R  b  ler *et al.*¹⁵ conducted on a single cylinder engine representative of a Euro VI commercial vehicle engine. In general, they found that parameters which decrease NO_x emissions lead to increases in NO_2/NO_x ratio. Table 1 shows the effect of common diesel engine parameters on NO_2/NO_x ratio according to R  b  ler *et al.*¹⁵ in ascending order of importance.

Table 1: Effect of common diesel engine parameters on NO_2/NO_x ratio¹⁵

Parameter	NO_x emission	NO_2/NO_x ratio
Humidity \uparrow	\downarrow	\uparrow
Inlet air temperature \uparrow	\downarrow	\uparrow
EGR rate \uparrow	\downarrow	\uparrow
Fuel pressure \uparrow	\downarrow	\uparrow
SOI \uparrow	\downarrow	\uparrow
λ \uparrow	\uparrow	\uparrow

Typically an SCR catalyst requires a 1:1 ratio of $\text{NO}:\text{NO}_2$ ¹⁶ for maximum efficiency because the ratio influences both the oxygen and ammonia needed to reduce NO_x and the speed of the reduction reaction¹⁷. Therefore an understanding of the NO/NO_2 split within the total NO_x is important. Diesel Oxidation Catalysts (DOCs) are often used to promote the formation of NO_2 to obtain this 1:1 ratio, however their conversion efficiency varies with temperature and DOC material, and under certain conditions DOCs may in fact promote formation of NO from NO_2 ^{16, 18}.

Hence, the $\text{NO}:\text{NO}_2$ ratio has a material effect on the efficiency of the exhaust aftertreatment system, and may be partially responsible for transient breakthroughs in NO_x . In modern aftertreatment systems, to ensure extremely low tailpipe NO_x emissions, it may be desirable to couple an SCR system as close as possible to the engine to ensure fast catalyst warm-up on engine start – meaning that such an SCR would be before any DOC fitted¹⁹. In such a case, careful control of the engine-out $\text{NO}:\text{NO}_2$ ratio would be essential.

NO_2 can also play a crucial role in the oxidation of soot collected on passive regeneration DPF systems; the temperature required to oxidise soot in NO_2 is approximately 250 °C whereas the temperature to oxidise soot in oxygen is 550 °C²⁰. The relevant equations for soot oxidation in NO_2 are:



It may be that at high levels of engine out NO_2 the associated levels of passive DPF regeneration would extend the intervals between active regenerations.

Given that Hilliard and Wheeler⁹ report NO_2 levels up to 30 % and Rößler *et al.*¹⁵ levels up to 20 % of total NO_x emitted from a diesel engine (on an engine out basis) it is important to understand what impact engine transients have on the $\text{NO} : \text{NO}_2$ ratio. Recent work has shown that the $\text{NO}_2 / \text{NO}_x$ ratio can vary quickly during drive cycle transients. NO , NO_x , and the $\text{NO}_2 / \text{NO}_x$ ratio measurements from a Euro 6 light duty diesel vehicle undergoing a Worldwide harmonized Light vehicles Test Cycle (WLTC) measured post-turbocharger (but before any aftertreatment) are shown in Figure 1²¹. A number of features can be seen here, for example NO_x production is stopped during fuel shut-offs during decelerations associated with gear changes and the measurements fall to zero at these times. There are also steps in NO_x immediately following these gear changes possibly associated with EGR delivery delay. Figure 1 also shows that the $\text{NO}_2 / \text{NO}_x$ ratio (excluding fuel shut-offs) varies between about 10 % and 70 % over this early part of the WLTC (where the engine is at moderate loads). This variation can take place very quickly during these transients. During the deceleration fuel shut-offs (where no combustion is occurring), the $\text{NO}_2 / \text{NO}_x$ ratio is meaningless and is displayed as around 100 %.

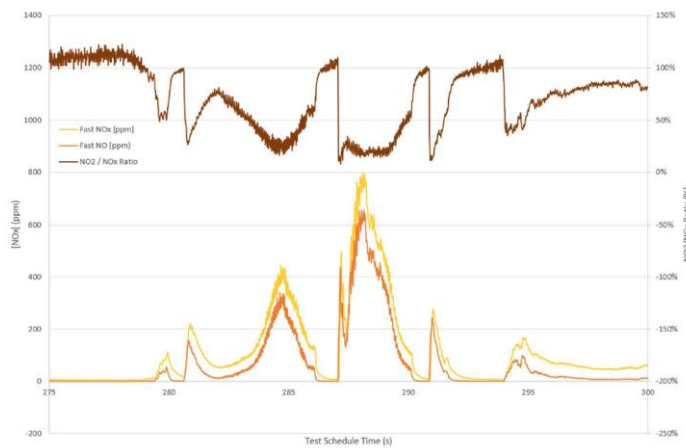


Figure 1: NO , NO_x and $\text{NO}_2 / \text{NO}_x$ ratio from a Euro 6 vehicle during a an early part of the WLTC²¹

It is clear that $\text{NO}_2 / \text{NO}_x$ ratios can vary widely and very rapidly over the engine operating range, but the cause of these variations is not completely understood. The recent comprehensive work by Rößler *et al.*¹⁵ was undertaken on a medium duty engine, and all at steady state. There is therefore a clear need to investigate transient engine out $\text{NO}_2 / \text{NO}_x$ ratios from a light duty diesel engine and this has been undertaken in this work.

Experimental methodology

In this work NO and NO_x measurements have been taken in the exhaust port of a 500 cc per cylinder diesel engine to understand the effect that transient engine load steps has on the NO₂/NO_x ratio. Details of the engine are shown in Table 2.

Table 2: Test engine details

Displacement / cylinder	500 cm ³
Piston bowl	Re-entrant
EVO	128 °atdcf
EVC	382 °atdcf
Fuel Pressure	2200 bar maximum

The engine was fitted with a Kistler 6046Asp-3-2 cylinder pressure transducer in the same cylinder from which the NO and NO_x measurements were taken. These three parameters, alongside others, were logged by an AVL IndiSet Advanced 642 at a resolution of 0.1 CAD (which is a frequency between 9 kHz and 15 kHz for the engine speeds tested). The engine was run on a standard diesel fuel compliant with EN590²², which contained no fuel bound nitrogen. The boost conditions, which are temperature and pressure controlled, are supplied by an external air compressor; the relative humidity of this air remains below 1 %. More details about the engine and test facility set-up can be found in Leach *et al.*²³.

The test conditions at which the engine was run are shown in Table 3. These conditions were selected such that a representative range of the engine operating map was covered, in particular to give conditions where high (light load, high EGR) and low (high load, no EGR) levels of NO₂/NO_x ratio are expected to be seen. Given that the purpose of this work was to understand how the NO₂/NO_x ratio changed in response to engine load transients, the engine was held at constant speed at each point by a dynamometer, and the engine load (nIMEP) was changed as a step input from a value of 50 % of the nominal (75 % at test point 4) to the nominal load. Details are shown in Table 3, and steps in both directions (lower to higher and higher to lower) were conducted, each step being undertaken three times.

Table 3: Engine test conditions

Test point	1	2	3	4	5
Engine speed (rpm)	1500	1500	2000	2000	2500
Lower nIMEP (bar)	1.9	3.45	6.15	19.4	8.85
Higher (nominal) nIMEP (bar)	3.8	6.9	12.3	25.8	17.7
Exhaust back pressure (barG)	0.31	0.84	2.0	2.9	2.7
Inlet air temperature (°C)	55	40	40	40	40
Coolant and oil temperature (°C)	90	90	90	90	90
EGR targets (%)	0 & 45	0 & 32	0 & 22	0	0 & 15

Closed loop fuelling control was used to maintain a constant nIMEP, which was derived from the pressure signal. The response of the engine to step demands in load can be seen in Figure 2 which shows the recorded nIMEPs of engine cycles as the load is stepped from 3.45 bar nIMEP to 6.9 bar nIMEP at test point 2. It can be seen that the engine response is instantaneous, with the load transition a clear “step”. The CoVs of nIMEP are 4.9 % at 3.45 bar nIMEP and 3.4 % at 6.9 bar nIMEP. This pattern of instantaneous response is typical for all of the points tested.

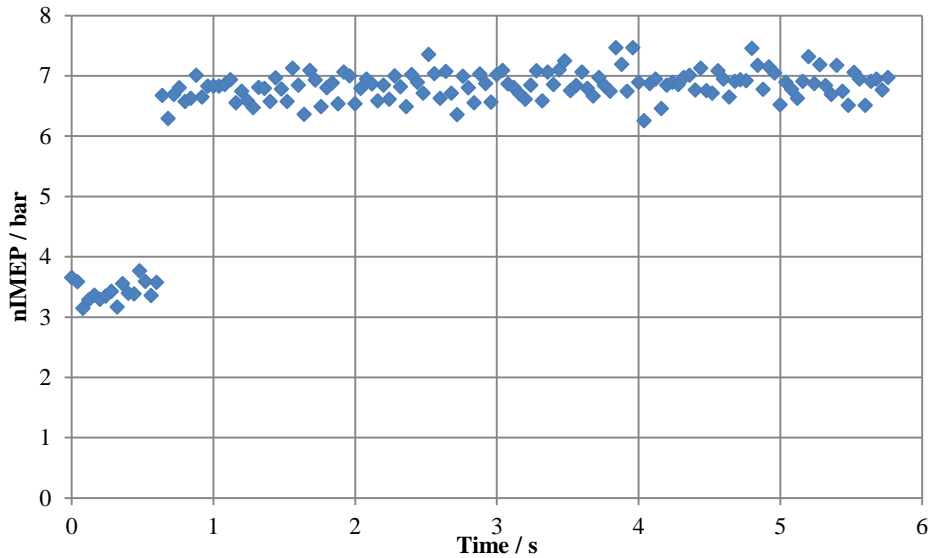


Figure 2: nIMEP for a load step up at test point 2. Each point represents the nIMEP of a single cycle

NO and NO_x measurements were made approximately 70 mm downstream of an exhaust port using a Cambustion CLD500^{24, 25} – although the engine is not fitted with a turbocharger, its effect is mimicked using an exhaust back pressure valve, and the sample is drawn at the exhaust back pressures shown in Table 3. The instrument was configured with its constant pressure heated sampling system to isolate the analyser from the temperature and pressure variations seen in the engine exhaust²⁶ and the sample is drawn very quickly using vacuum pumps to ensure a fast time response. Here, two CLD500 channels were used one measure NO directly, and the other passing the sample through a stainless steel NO_x converter (to convert NO₂ to NO), to measure total NO_x – a new NO_x converter was fitted at the start of these experiments to ensure 100 % conversion. As a result, in this work, NO_x is defined as: NO_x = NO + NO₂ and the contribution of N₂O (which as an engine out emission, can be assumed to be near zero – its presence in tailpipe emissions being due to reactions in the SCR²⁷) is ignored. The T_{10-90%} response time of the NO channel is 2 ms and of the NO_x channel - 10 ms. As a result the signals are time aligned. In addition, due to different exhaust flow rates and exhaust pressures

(inevitably higher flow rates and pressures give faster response times) the signals are also time aligned with respect to engine TDC. Full details on the time alignment is included in Leach *et al.*²⁸.

An example raw signal showing the NO and NO_x emissions from 6 cycles can be seen in Figure 3. These raw signals are corrected for quench in the chemiluminescence detector as well as for any drift observed (the analyser was recalibrated after each test point had been run). Figure 3 also shows the sampling windows that have been used to obtain the cycle averages shown in subsequent figures (these correspond to EVO and EVC).

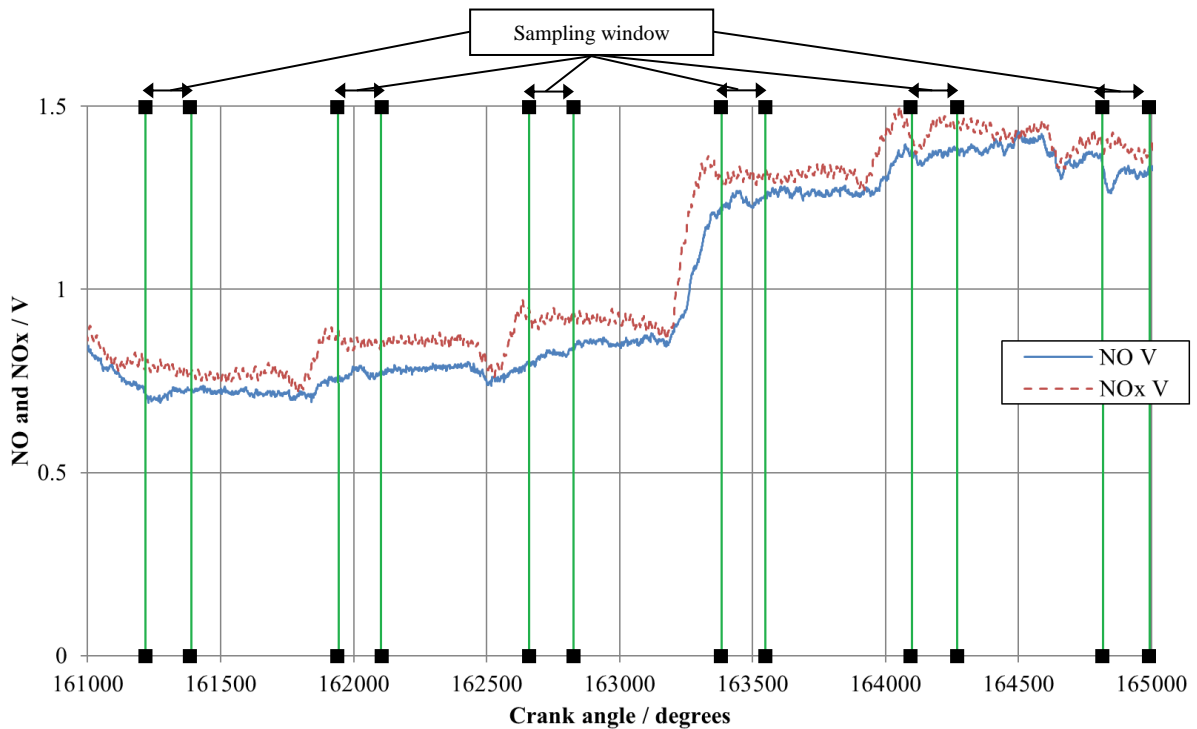


Figure 3: Example raw CLD500 signal at test point 3 showing sampling window for individual cycles

The crank angle resolved NO and NO_x emissions from 145 cycles were analysed for each test. The load step was commanded a short while after the signals had started to be logged - typically 20-50 cycles. This results in there being more cycles logged after the load step (100-130 cycles), than before – this was done partly to ensure that any post-step transients were captured. The consequence of this is that there are more data points in the post-step averages than in the pre-step averages. At test points with EGR, the load step resulted in a change in exhaust pressure (an increase for a step up, and decrease for a step down) and, because in this case EGR is driven by the pressure difference across the engine, this leads to a change in the EGR rate after a certain period. As a result, the change in EGR rate leads to a change in the NO and the NO_x emitted, and hence these signals are curtailed once the change in EGR has been observed.

In addition to these “fast” measurements, the standard emissions were measured using a Horiba MEXA-ONE emissions analyser, known as the “slow” analyser in this work. The sample for this is taken downstream of both the exhaust backpressure valve and a smoothing tank and as a result its time response is significantly slower. The “slow” analyser also uses the wet chemiluminescence method to measure NO and NO_x and the NO channel has a T_{10-90%} response time of 1.2 s and the NO_x channel a T_{10-90%} response time of 1.5 s, however in addition to these response times, the additional path length and mixing (in the smoothing tank) gives a total time response to engine outputs of around 15 s. These “slow” emissions and other measurement data were logged using Sierra-CP Cadet software at 1 Hz.

For both “fast” and “slow” analysers the NO₂ / NO_x ratio has been calculated as:

$$\frac{NO_x - NO}{NO_x}$$

Where NO or NO_x emissions have been presented in this paper, they have been rescaled by dividing by a nominal value, chosen such that the highest NO_x emissions give a value of around 1.

Results and discussion

Figure 4 shows the NO_x emissions from individual engine cycles as the engine undergoes a load step up at test point 2 – three separate runs (repeats) are shown. Each point on the graph represents the NO_x emitted from a single engine cycle. The NO_x emissions from the engine follow the step response in load exactly – with this “fast” NO_x sampling, it can be seen that as the engine nIMEP is stepped, the response in NO_x emissions from the engine is similarly instantaneous. This is to be expected, as the response of the engine nIMEP to the load demand as seen in Figure 2 is instantaneous, so it can be assumed that the engine thermal conditions also follow a similarly instantaneous response – and hence the step change in NO_x formation observed. It can also be seen that there is excellent repeatability between the three runs both before and after the step. Both this response and this repeatability are indicative of all of the runs undertaken, where excellent repeatability is observed throughout. The cycle-to-cycle variation in NO_x measured is almost entirely caused by cycle-to-cycle variations in the engine; the NO_x emitted from a cycle being closely correlated with the P_{Max} from that cycle as discussed in Leach *et al.*²⁸.

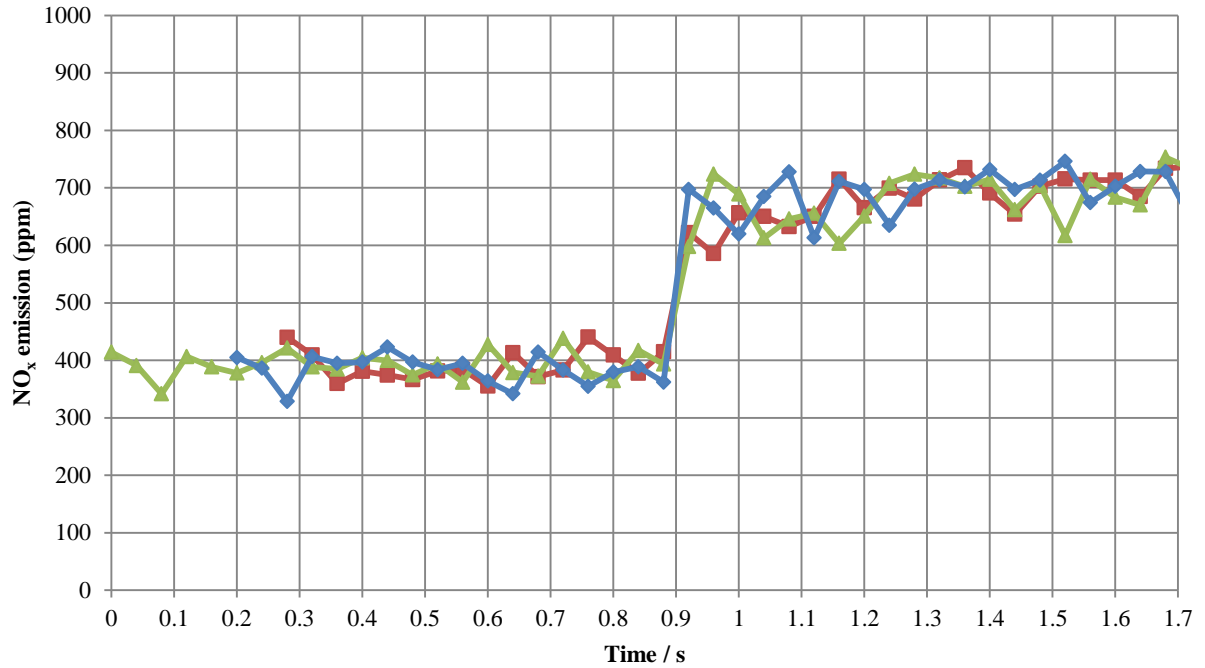


Figure 4: *NO_x emissions from a load step up at test point 2. Each point represents the NO_x emissions from a single cycle*

Figure 5 shows the NO₂/NO_x ratio for individual cycles for the same tests as shown in Figure 4 as the engine undergoes a load step up at test point 2. Again each point represents the NO₂/NO_x ratio from a single cycle and three separate runs (repeats) are presented. There is more noise observed in this signal because the NO₂/NO_x ratio is derived by combining two already noisy signals, so the noise is similarly increased, however all of this noise can be attributed to cycle-to-cycle variations in the engine, as discussed above. As would be expected, as the NO and NO_x emissions have an instantaneous response to the engine load step, the NO₂/NO_x ratio has a similarly instantaneous response with the NO₂/NO_x ratio moving from about 0.11 to 0.05 across the load step. Again, very good repeatability between the three runs is observed with the repeats all falling within the cycle-to-cycle variations observed.

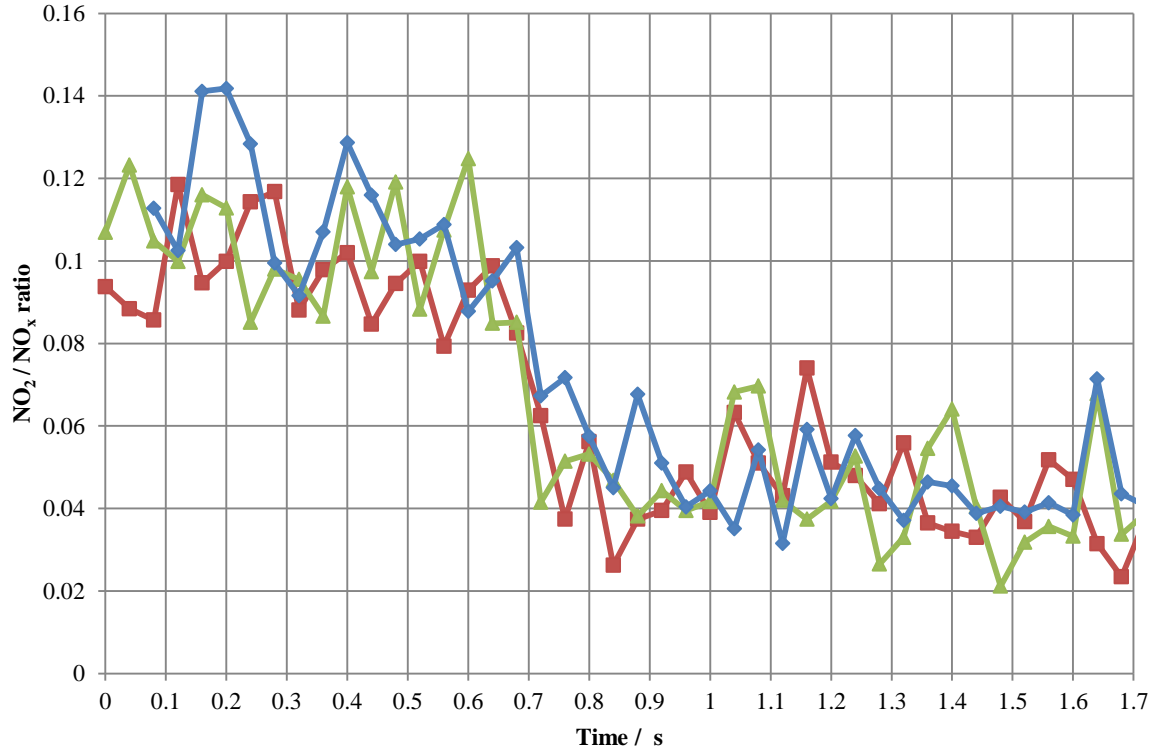


Figure 5: NO_2/NO_x ratio from a load step up at test point 2. Each point represents the ratio emitted from a single cycle

Figure 6 shows the NO_2/NO_x ratios for the load steps undertaken without EGR. The load steps up are shown as solid lines, and the steps down as dashed lines; the arrows indicate the direction of the change in load and the NO_2/NO_x ratio. Each point is the average of the three experimental runs with the error bars corresponding to the standard deviation (σ) of those three runs. It can be seen that as the engine load decreases the NO_2/NO_x ratio increases, with ratios as high as 0.2 observed at the lightest loads – where the quenching of the flame will be taking place before the $\text{NO}_2 \rightarrow \text{NO}$ reaction has been completed. At the highest loads (test point 4) there is no difference in the NO_2/NO_x ratio as the load is changed. This would suggest at this test condition, the in cylinder temperatures remain high enough to drive the $\text{NO}_2 \rightarrow \text{NO}$ reaction to completion at both the lower and the higher load (the NO_2 levels here are essentially zero). All of these levels are in agreement with the work undertaken by Rößler *et al.*¹⁵. It is also noted that the NO_2/NO_x ratio is consistent at a given load regardless of whether that load has been reached by a step up or a step down.

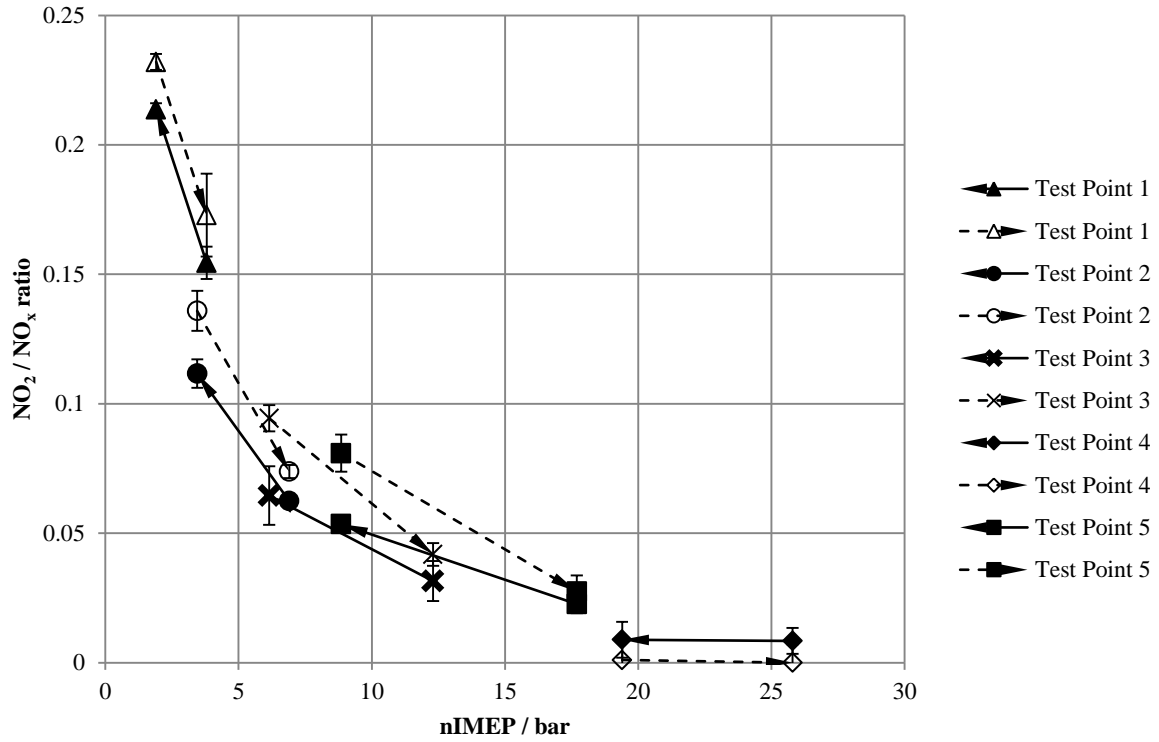


Figure 6: NO_2/NO_x ratio for load steps up (solid lines) and down (dashed lines) without EGR. The error bars correspond to $\pm \sigma$

Figure 7 shows similar results to Figure 6 but for the test points with EGR (note test point 4 was not run with EGR). It can be seen that high levels of NO_2/NO_x ratio are seen at the test points with EGR – this is consistent with EGR reducing combustion temperatures and hence quenching the reactions earlier, leading to the $\text{NO}_2 \rightarrow \text{NO}$ reaction not being completed and higher levels of NO_2 . At the lightest loads, instantaneous responses of around 20 % in NO_2/NO_x ratio are observed to step changes in load. However, when EGR is applied, the NO_2/NO_x ratio is not as consistent at a given load regardless of whether that load has been reached by a step up or a step down as it was at test points without EGR – notably at the lightest loads. Looking at the results in detail, these inconsistencies are attributed to the fact that despite careful targeting, the overall measured EGR levels achieved at this test point vary between 41 % and 47 %, and this variability is leading to a difference in the NO_2/NO_x ratio. In addition the observed NO and NO_x levels are very low at these test points, and so the measurement accuracy of the analysers, as well as the signal to noise ratio is not as good.

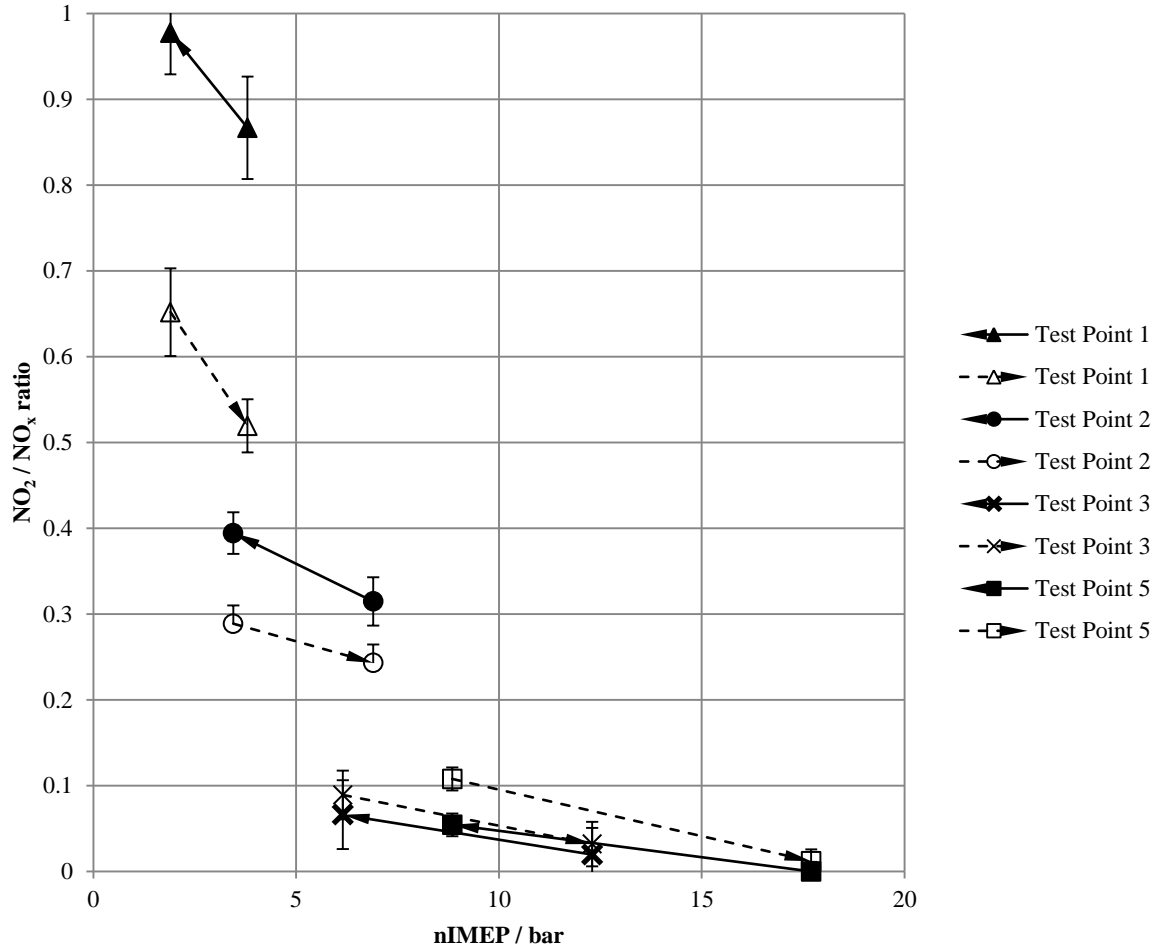


Figure 7: NO_2/NO_x ratio for load steps up (solid lines) and down (dashed lines) with EGR. The error bars correspond to $\pm \sigma$

Comparison between analysers

Figure 8 shows the comparison between the measured NO and NO_x emissions from the “fast” and “slow” analysers. A very good agreement can be seen between the two sets of measurements ($R^2 = 0.98$ for both NO and NO_x), giving confidence that the “fast” measurements are equivalent to those measured by the standard “slow analyser”. However, the “fast” analyser gives approximately 8 % higher readings for NO_x and 10 % higher readings for NO. Figure 8 also shows the variability within each measurement point (the error bars correspond to $\pm \sigma$), and it is seen that the variability of the “fast” analyser is greater than that of the “slow” analyser (in general the error bars for the “slow” analyser are smaller than the data points for that analyser). This is because the “fast” analyser is measuring the cyclic variability of the NO and NO_x emissions (as was observed in Figure 4 and discussed in Leach *et al.*²⁸), which are not observed by the “slow” analyser.

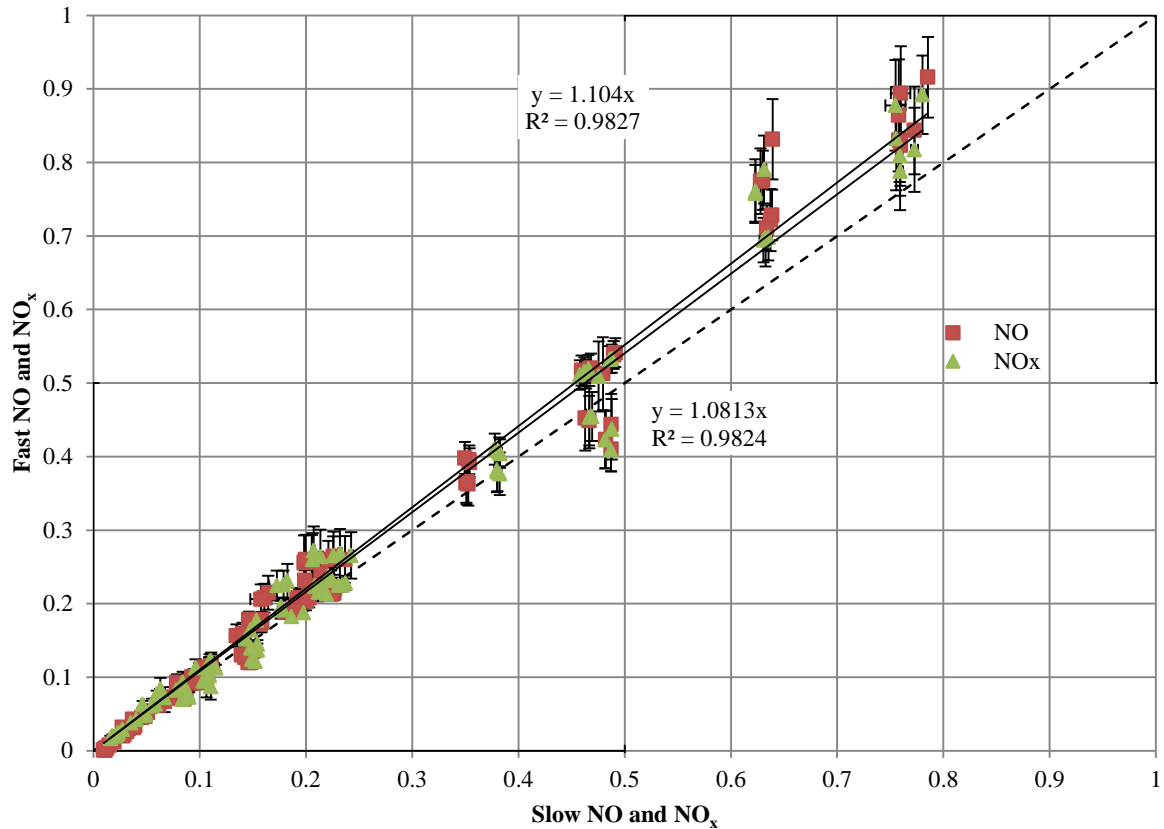


Figure 8: Comparison between fast and slow NO and NO_x measurements. The error bars correspond to $\pm \sigma$, the dashed line to the unity slope

Understanding why the “fast” analyser reads a higher NO and NO_x value than the “slow” is clear from Figure 9. Figure 9 shows the time aligned NO and NO_x emissions from the “fast” and “slow” analysers at test point 3. Initially, the agreement between the two analysers is good, although the fast analyser is picking up the cycle-to-cycle variation which the slow analyser does not observe – so the fast analyser appears noisier. When the load-step happens, the different response times of the analyser measurements are clearly seen. The “slow” analyser takes around 6 s to reach steady state value after the step, whereas the response of the “fast” analyser is instantaneous (i.e. much less than the time between engine cycles) – note that this is likely to be due to a combination of the slower response of the analyser, the longer path to the “slow” analyser, and greater mixing length in the engine exhaust before the “slow” analyser sample point. In addition, the delay caused by the NO_x converter on the “slow” NO_x channel means that during the transient, there is more NO measured than NO_x by the “slow” analyser – clearly not a real result. Given the near-instantaneous response of the “fast” analyser, and the mixing experienced by the “slow” analyser, the smoothing of the results means that the “slow” analyser

misses the peak value of NO and NO_x that the “fast” analyser observes, and hence the apparent over-reading of the “fast” analyser is in fact likely to be an under-read of the “slow” analyser.

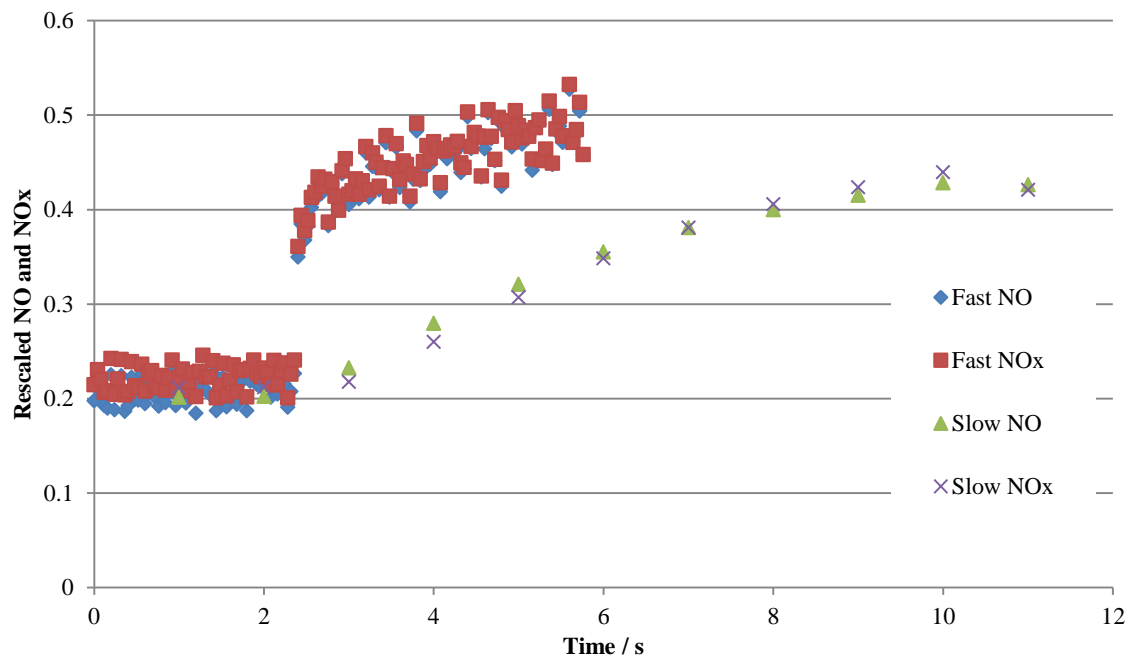


Figure 9: NO and NO_x emissions during a load step up at test point 3 showing response of fast and slow analysers

Figure 10 shows the comparison between the measured NO₂/NO_x ratio from the “fast” and “slow” analysers. Here, in general a good agreement can be seen between the two different measurements, as would be expected given the good correlation between the analysers in the NO and NO_x emissions. There are a small number of points (circled on Figure 10) where there is substantial deviation from the unity slope, with the “fast” analyser giving values that are up to double that of the “slow” analyser. These points are all at test point 1 at high levels of EGR.

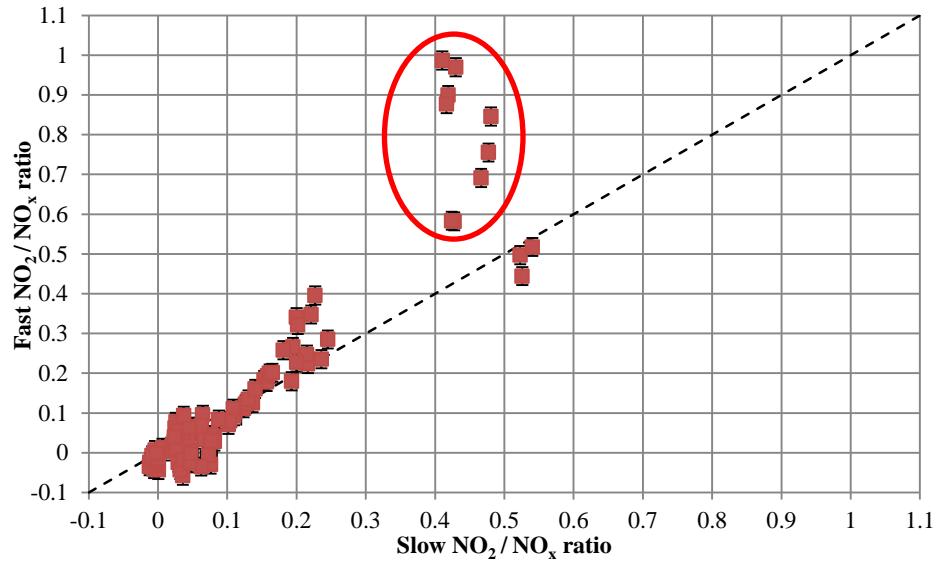


Figure 10: Comparison between fast and slow NO₂/NO_x ratios. The error bars correspond to $\pm \sigma$, the dashed line to the unity slope

Figure 11 shows the “fast” and “slow” NO and NO_x emissions as well as the NO₂/NO_x ratios derived from those signals at test point 1, 45 % target EGR. This is one of the points circled in Figure 10 where the agreement between the “fast” and “slow” analysers is poor. It can be seen that there is good agreement between the NO_x readings of the two analysers; however there is a difference in the NO readings. The overall levels of NO and NO_x are very low indeed overall, practically zero in both cases, particularly in the case of NO, so apparent large difference in the NO₂/NO_x ratios is in fact due to the overall low levels, and a minor difference in NO – which at higher levels of NO emissions would be unimportant. Both analysers claim a 1 % of full scale accuracy, and indeed this difference is well within those limits for both analysers and beyond their measurement capabilities.

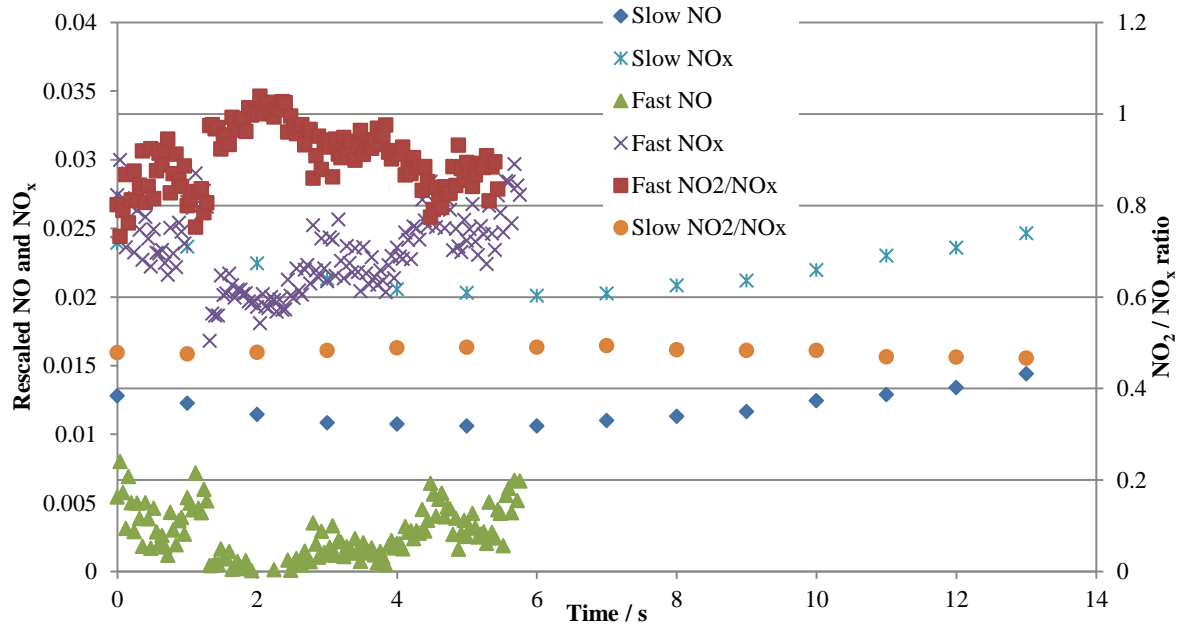


Figure 11: NO, NO_x and NO₂/NO_x ratio from fast and slow analysers at test point 1, 45 % target EGR, load step up

Conclusions

In this work engine-out NO and NO_x (here defined as NO + NO₂) emissions have been measured on a cycle-to-cycle basis from a high speed light duty diesel engine using an emissions analyser with a very fast time response. These measurements have been used to derive cyclic NO₂/NO_x ratios. These NO₂/NO_x ratios have then been evaluated as step changes in load are demanded from the engine at constant speed with all other engine parameters held constant. The results show that:

1. The NO₂/NO_x ratios observed in this work are in line with previously reported results, albeit with high levels observed at the very lightest loads which have not been reported in the open literature to the authors' knowledge. These high NO₂/NO_x ratios are due to high levels of EGR and light loads leading to low combustion temperatures which suppress the NO₂ → NO reaction – these conditions also lead to very low overall levels of NO_x being emitted.
2. The response in NO_x levels and NO₂/NO_x ratios to step changes in engine load are instantaneous, suggesting that the in cylinder conditions change similarly instantaneously. No significant transient effects were observed following the step change.
3. The “fast” and the “slow” analysers showed good agreement, having taken into account their differing response times.

4. The response of the “slow” analyser to the step-change in engine load may appear as a transient, however the “fast” analyser reveals that the change in engine-out emissions is instantaneous, the appearance of a transient is caused by the response time of the “slow” analyser.

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Nomenclature

CAD	Crank Angle Degree
CFD	Computational Fluid Dynamics
CLD	ChemiLuminescence Detector
DOC	Diesel Oxidation Catalyst
EGR	Exhaust Gas Recirculation
EVO	Exhaust Valve Opening
EVC	Exhaust Valve Closing
LNT	Lean NO _x Trap
nIMEP	net Indicated Mean Effective Pressure
NO _x	Oxides of Nitrogen
P _{Max}	Maximum Cylinder Pressure
RDE	Real Driving Emissions
SCR	Selective Catalytic Reduction
SOI	Start of Injection
TDC	Top Dead Centre

References

1. Chung J, Kim H and Sunwoo M. Reduction of transient NO_x emissions based on set-point adaptation of real-time combustion control for light-duty diesel engines. *Applied Thermal Engineering*. 2018; 137: 729-38.
2. Johnson TV. Diesel Emissions in Review. *SAE Int J Engines*. 2011; 4: 143-57.
3. Johnson TV. Review of Vehicular Emissions Trends. *SAE Int J Engines*. 2015; 8: 1152-67.
4. Groß A, Beulertz G, Marr I, Kubinski DJ, Visser JH and Moos R. Dual mode NO_x sensor: Measuring both the accumulated amount and instantaneous level at low concentrations. *Sensors*. 2012; 12: 2831-50.
5. Hagen JR, Assanis DN and Filipi ZS. Cycle-resolved measurements of in-cylinder constituents during diesel engine transients and insight into their impact on emissions. *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*. 2011; 225: 1103-17.
6. Heywood JB. *Internal combustion engine fundamentals*. McGraw-hill New York, 1988.
7. Stone R. *Introduction to internal combustion engines*. Palgrave Macmillan, 2012.
8. Merryman EL and Levy A. Nitrogen oxide formation in flames: the roles of NO₂ and fuel nitrogen. *Symposium (international) on combustion*. Elsevier, 1975, p. 1073-83.
9. Hilliard JC and Wheeler RW. Nitrogen Dioxide in Engine Exhaust. SAE International, 1979.

10. Yu X, Yu S and Zheng M. Hydrocarbon impact on NO to NO₂ conversion in a compression ignition engine under low-temperature combustion. *International Journal of Engine Research*. 2017; 1468087417745441.
11. Lee S, Lee Y, Kim G and Min K. Development of a Real-Time Virtual Nitric Oxide Sensor for Light-Duty Diesel Engines. *Energies*. 2017; 10.
12. Hoon C, Brien F, Devesh U, Thomas B and Michiel van N. In-cylinder pressure sensor-based NO_x model for real-time application in diesel engines. *International Journal of Engine Research*. 2017; 19: 293-307.
13. Leach F, Ismail R, Davy M, Weall A and Cooper B. The effect of a stepped lip piston design on performance and emissions from a high-speed diesel engine. *Applied Energy*. 2018; 215: 679-89.
14. Leach F, Ismail R and Davy M. Engine-out emissions from a modern high speed diesel engine – The importance of Nozzle Tip Protrusion. *Applied Energy*. 2018; 226: 340-52.
15. Rößler M, Velji A, Janzer C, Koch T and Olzmann M. Formation of Engine Internal NO₂: Measures to Control the NO₂/NO_x Ratio for Enhanced Exhaust After Treatment. *SAE Int J Engines*. 2017; 10: 1880-93.
16. Stadlbauer S, Waschl H, Schilling A and del Re L. DOC Temperature Control for Low Temperature Operating Ranges with Post and Main Injection Actuation. SAE International, 2013.
17. Iwasaki M and Shinjoh H. A comparative study of “standard”, “fast” and “NO₂” SCR reactions over Fe/zeolite catalyst. *Applied Catalysis A: General*. 2010; 390: 71-7.
18. Czerwinski J, Zimmerli Y, Chiesura C, Mayer A, Lemaire J and D'Urbano G. NO₂-Formation in Diesel Particle Filter Systems. SAE International, 2013.
19. Cloudt R, Baert R, Willems F and Vergouwe M. SCR-only Concept for Heavy-duty Euro VI Applications. *MTZ worldwide*. 2009; 70: 58-63.
20. Allansson R, Blakeman PG, Cooper BJ, Hess H, Silcock PJ and Walker AP. Optimising the Low Temperature Performance and Regeneration Efficiency of the Continuously Regenerating Diesel Particulate Filter (CR-DPF) System. SAE International, 2002.
21. Cambustion. Application note: Transient NO₂:NO_x ratio. 2016.
22. British Standards BS EN 590 Diesel, Requirements and Test Methods. 2009.
23. Leach F, Ismail R, Davy M, Weall A and Cooper B. Comparing the Effect of Fuel/Air Interactions in a Modern High-Speed Light-Duty Diesel Engine. *SAE Technical Paper 2017-24-0075*. 2017.
24. Reavell KSJ, Collings N, Peckham M and Hands T. Simultaneous Fast Response NO and HC Measurements from a Spark Ignition Engine. SAE International, 1997.
25. Schurov S, Collings N, Hands T, Peckham M and Burrell J. Fast Response NO/HC Measurements in the Cylinder and Exhaust Port of a DI Diesel Engine. SAE International, 1998.
26. Leach FCP, Davy MH, Siskin D, Pechstedt R and Richardson D. An optical method for measuring exhaust gas pressure from an internal combustion engine at high speed. *Review of Scientific Instruments*. 2017; 88: 125004.
27. Cho CP, Pyo YD, Jang JY, Kim GC and Shin YJ. NO_x reduction and N₂O emissions in a diesel engine exhaust using Fe-zeolite and vanadium based SCR catalysts. *Applied Thermal Engineering*. 2017; 110: 18-24.
28. Leach F, Davy M and Peckham M. Cycle-to-Cycle NO & NO_x emissions from a HSDI engine. *ASME 2018 Internal Combustion Fall Technical Conference*. San Diego, CA, USA: ASME, 2018.