CZECH TECHNICAL UNIVERSITY IN PRAGUE

Faculty of Mechanical Engineering

Department of Automotive, Combustion Engine and Railway Engineering

MASTER THESIS

Detection of excess NO_x emissions of Heavy vehicles during ordinary operation

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Submitted by : Alden Fred Arul Raj

Supervisor : doc. Michal Vojtíšek, Ph.D

MASTER'S THESIS ASSIGNMENT

I. Personal and study details

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Study program: **Master of Automotive Engineering**

Branch of study: **Advanced Powertrains**

II. Master's thesis details

Master's thesis title in English:

Detection of excess NOx emissions of heavy vehicles during ordinary operation

Master's thesis title in Czech:

Detekce nadměrných emisí oxidů dusíku u těžkých vozidel během běžného provozu

Guidelines:

This experimental thesis addresses the contribution of high emitters to the nitrogen oxides (NOx) emissions from transport, as a part of the broader effort to reduce adverse health effects associated with outdoor air pollution. The goal of the thesis is to explore the possibility of detecting vehicles with excess NOx by using a chase vehicle equipped with a fast-response gas analyzer. Emission factors will be estimated based on NOx/CO2 ratio in the plume and compared to the anticipated emissions based on the vehicle data obtained from the vehicle registry or from the electronic toll system. The student is expected to participate in experimental campaigns targeting instrument validation and/or pilot measurements in the Prague vicinity, and to evaluate the results from a pilot study with the focus on assessing the emissions performance of newer heavy duty trucks equipped with NOx aftertreatment devices. The thesis should contain relevant background information, statistical analysis of the data including assessment of measurement uncertainty, and a discussion on differentiating normal operation from 'excess' emissions.

Bibliography / sources:

CANAGARATNA, Manjula R., et al. Chase studies of particulate emissions from in-use New York City vehicles. Aerosol Science and Technology, 2004, 38.6: 555-573.
HALLQUIST, Å. M., et al. Particle and gaseous emissions from individual diesel and CNG buses. Atmospheric Chemistry and Physics, 2013, 13.10: 5337-5350.

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Date of master's thesis assignment: **11.09.2019** Deadline for master's thesis submission: **10.01.2020**

Assignment valid until: _____

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Supervisor's signature	Head of department's signature	Dean's signature

III. Assignment receipt

The student acknowledges that the master's thesis is an individual work. The student must produce his thesis without the assistance of others, with the exception of provided consultations. Within the master's thesis, the author must state the names of consultants and include a list of references.

Date of assignment receipt _____ Student's signature _____

Declaration of authorship

I hereby declare, that this diploma thesis has been written by me in person. All the information from other works has been acknowledged in the text with the list of references.

In Prague: 08. 01. 2020

_____

Alden Fred Arul Raj

Anotace

Diplomová práce se zabývá vyhodnocením výsledků měření emisí NO_x ze silničních nákladních vozidel během jízdy po dálnici. Měření bylo provedeno měřicím vozidlem vybaveným infračerveným analyzátorem plynů s rychlou odezvou, který vzorkoval vlečku výfukových plynů ze sledovaného vozidla. Poměr koncentrací NO a CO_2 ve vlečce byl stanoven třemi způsoby: lineární regresí, numerickou integrací naměřených koncentrací, a jako poměr maximálních naměřených koncentrací, vždy po stanovení a odečtu pozaďových koncentrací. Tyto způsoby jsou porovnány. Z poměru NO/CO_2 byl vypočten emisní faktor v g/kWh NO, který byl porovnán s emisními limity pro Euro kategorii měřeného vozidla, která byla vyčtena ze systému elektronického mýtného. Práce byla součástí projektu, jehož cílem je posoudit míru výskytu nákladních vozidel s nadměrnými emisemi NO_x.

Klíčová slova: vznětový motor, těžká silniční vozidla, nákladní automobily, oxidy dusíku (NO_x), selektivní katalytická redukce, emisní factor, vzdálené měření, emise v provozu, FTIR, SCR emulator, technický stav, znečištění ovzduší, zpracování dat.

Abstract

This master thesis deals with the detection of excess NO_x emissions from heavy duty vehicles on road by using a "vehicle chase method" in which the chase vehicle is equipped with a fast-response gas analyzer to detect the emissions. Emission factor is evaluated based on the ratio of NO/CO_2 in the plume determined by linear regression approach, peak area approach and maximum point of concentration approach. Measured data were analyzed by creating baseline, identifying peak, evaluation of detection limit with some uncertainties in the measurement. Detection limit is set by taking the standard deviation of the background signal and multiplied by a factor to consider the concentrations above this limit as a useful measurement for analysis. The results of this evaluation are summarized to detect the higher concentration of NO through different approaches and are checked for consistency between these approaches.

Keywords: Diesel engine, heavy-duty vehicle, Nitrogen oxides (NO_x), Selective Catalytic Reduction, emission factor, real-world emissions, high emitter, FTIR, chase vehicle, SCR emulator, in-use compliance, air quality, data analysis.

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Content

1 Introduction

Global and local air pollution, especially the emissions from transportation sources have vast range of impacts like smog formation, global warming, visibility degradation and several health effects for human and environment. Air is one of the main sources in the atmosphere for a living being to survive. If air in the atmosphere is polluted by major emissions and pollutants, then the living being in this environment are going to be destroyed.

Particles and NO are the major harmful pollutants from the transportation source which causes air pollution which is hazardous to environment and human health [1]. Though particles are dangerous pollutant than NO_x from internal combustion engines which has a vast influence on the air quality [2], concentration of NO_x emitted from heavy duty vehicle is considered for measurement and analysis in this thesis work. According to WHO, any contaminants in the atmosphere that affects human, animal and plant life is described as air pollution.

Emissions are from various sources, but transportation source contributes major portion of emission in our daily life [3]. Nowadays, significant increase of vehicles passing on the road results in increase of pollution. As we are approaching to clean, ecofriendly and sustainable mobility, NO_x emission from the vehicles are one of the major issues concerning human health and the environment. Due to new legislation and emission limits, concentration level in the exhaust emissions are reduced over the years. Mobile sources have harmful effects on the quality of air. But these emissions are difficult to predict as many parameters affect these measurements and creates variability in emission measurement from different type of vehicles [4].

1.1 Oxides of Nitrogen (NO_x)

NO_x is not a single compound, but a mixture of gases that are composed of Nitric Oxide (NO) and Nitrogen Dioxide (NO_2). NO_x is responsible for large share of health effects which are present in the exhausts of the majority of transportation sources like motor vehicles, lawn mowers, shipping, railways and airways, industrial source like electric supply, manufacturing, oil and gas industry, cigarette smoking and consumer source like nitrate containing fertilizers [5].

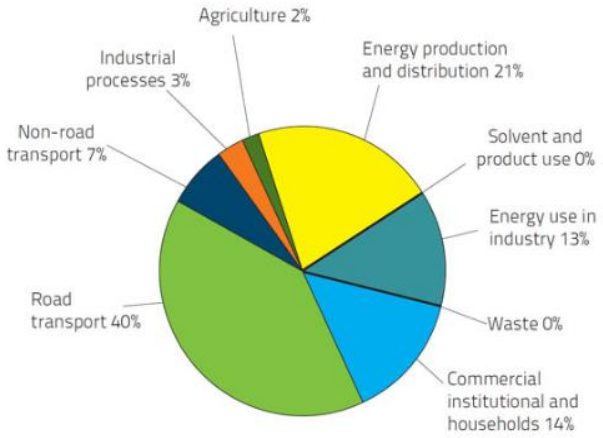

Fig 1. 1 Major sources of NO_x emissions in the EU during 2011 [3].

NO is a colorless and odorless gas. NO_2 is a highly reactive gas which has odor and has a high oxidizing property. NO_2 has around five times higher toxic and harmful effects than NO [6]. The concentration of NO is found to be higher in the areas of congested motor vehicle traffics, large cities and in majority of parking areas. Whenever a combustion happens in the presence of Nitrogen and oxygen at a high temperature, NO is formed - for example in engines and burning of some plant material and during lightning [3].

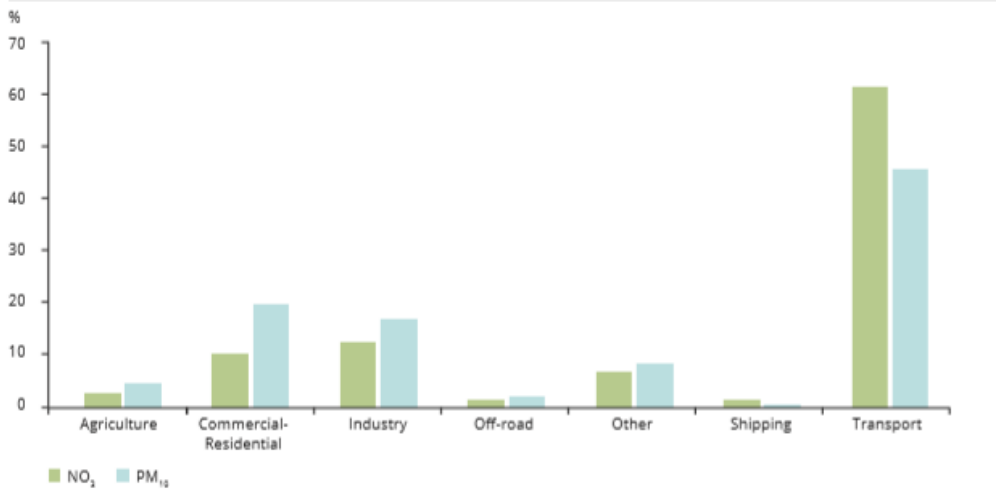

Fig 1. 2 Various sectors of NO_2 and Particulate Matter contribution reported by EU-28 Member states [7]

The above *figure 1.2* clearly shows that the major contribution of NO_2 and Particulate Matters are from Transport as reported by 28 member states of European Union, which is not good news for human health and environment.

1.1.1 NO_x Formation

Air in the atmosphere has 78.6% of Nitrogen and 21% of Oxygen. At high temperatures, more than 1800 K, molecular Nitrogen (N_2) disassociate into its atomic state (N), Also Oxygen (O_2) dissociates to atomic Oxygen [8].

NO_x formation are basically three equations of Zeldovich extended mechanism which is represented as follows

$$N_2 + O = NO + N$$

$$N + O_2 = NO + O$$

$$N + OH = NO + H$$

The first two equations of NO formation reactions were suggested by Zeldovich and later Lavoie added the third reaction to this mechanism and so this model is together called Zeldovich extended mechanism [9]. NO reaction is very slow, and it requires quite a high temperature for its formation. Similarly, NO_2 occupies several % of total oxides of Nitrogen released during the exhaust from the diesel engine in which 10 - 30% are found after Diesel Oxidation Catalyst (DOC). NO_2 are rapidly formed from NO in the flame zone region at a high temperature. Due to local quenching and cooling, NO_2 formed in the first reaction are cooled down and dissociates to form NO. The formation of NO_2 is represented in the following equations [9].

$$NO + HO_2 = NO_2 + OH$$

$$NO_2 + O = NO + O_2$$

Formation of NO are kinetically driven by temperature and enough Oxygen. Their chemical reactions are very slow at high temperatures and will never attain equilibrium which is a major disadvantage. Though Diesel engines are globally running in lean mixture, they can have a very high local temperatures inside the cylinder because of inhomogeneity in Air fuel mixtures. So, it's very complex to explain the processes happening inside the cylinder. But certain detailed studies and research have said that the rate of formation of NO_x is mostly at the kinetic phase of combustion where the mixing of Air and fuel takes place predominantly and the occurrence of initial rapid combustion results in enormous amount of temperature.

When the combustion duration is longer, rate of formation of NO is higher corresponding to high temperature Burnt gases.

Boltzman exponential factor is an important term to show the probability of formation of NO in the Arhenius equation. Higher the temperature, higher is the exponential factor which tends to increase the rate of concentration (K) or formation of NO. Arhenius equation to represent the rate of the reaction is

$$K = A \exp^{-(Ea / RT)}$$

Where, K = Rate constant for the reaction R = Gas constant (KJ/Kg-K)

A = Pre-exponential factor E_a = Activation Energy (KJ/Kg)

T = Temperature (K)

At high temperatures (thermodynamic part) and probability of availability of enough Oxygen, rate of formation of NO_x is enormous [9]. When the engine is operating in too lean, which means there's too much Oxygen which freezes the chemistry and there is reduction in the formation of NO_x as there is no enough temperature. Generally, NO_x is dominant in Indirect injection engine compared to Direct injection engine, since Indirect Injection Engine as high compression ratio which thereby increases the combustion temperatures [10].

1.1.2 Methods to reduce NO_x

NO_x exhausted to atmosphere can be possibly reduced by two ways 1. By In-cylinder techniques in reducing the formation of NO_x and 2. By some other after - treatment devices before the exhaust gases are released to atmosphere.

1. As NO_x is mainly formed due to higher combustion temperature inside the cylinder, time factor also plays a major role for the formation of NO_x. During the combustion process, reducing the peak temperature decreases the amount of NO_x, whereas this influences the rate of reaction, slower or faster combustion duration and increase in particulate emissions and other pollutants like carbon monoxide (CO) and unburnt hydrocarbons (UHC). So, to reduce this harmful NO_x, various techniques like Low Temperature Combustion (LTC), Homogeneous Charge Compression Ignition (HCCI), Homogeneous Charge Late Injection (HCLI), Highly Premixed Late Injection (HPLI), Reaction Controlled Compression Ignition (RCCI) and Premixed Charge Compression Ignition (PCCI) [11] were developed.

These techniques were achieved mostly only in research engines or in experimental engines and it's very difficult to implement and achieve those performance in practical engines in the market. Apart from these, other possible ways to reduce the formation of NO_x are Exhaust Gas Recirculation (EGR) which decreases the peak in-cylinder temperature by sending back a portion of exhaust gases or much more in to intake, Water injection, retarded and split fuel injection [8], where the fuel is injected at the late phase of power stroke, decreases the thermodynamic efficiency which increases other pollutants like HC and CO, but decreases NO.

2. Some after treatment devices which are used to reduce the formation of NO_x are Lean NO_x Trap (LNT) which performs effectively by alternative lean and rich mixtures. NO_x can also be further reduced by Non-Selective catalytic reduction (NSCR) and by Selective catalytic Reduction (SCR).

1.1.3 Lean NO_x trap (LNT)

NOx storage/reduction (NSR) or LNT mechanism works with the help of catalysts that contains three main components: (a) catalytically active noble metals like Platinum, Palladium and Rhodium for performing oxidation and reduction reactions, (b) NO_x storage material like Barium oxide and (c) an oxidic high surface area support (CeO_2, ZrO_2, Al_2O_3) [12]. The active surface of Pt oxidizes NO to NO_2 and these Nitrates are stored further and reduces to N_2. This mechanism is schematically shown in the *Figure 1.3.*

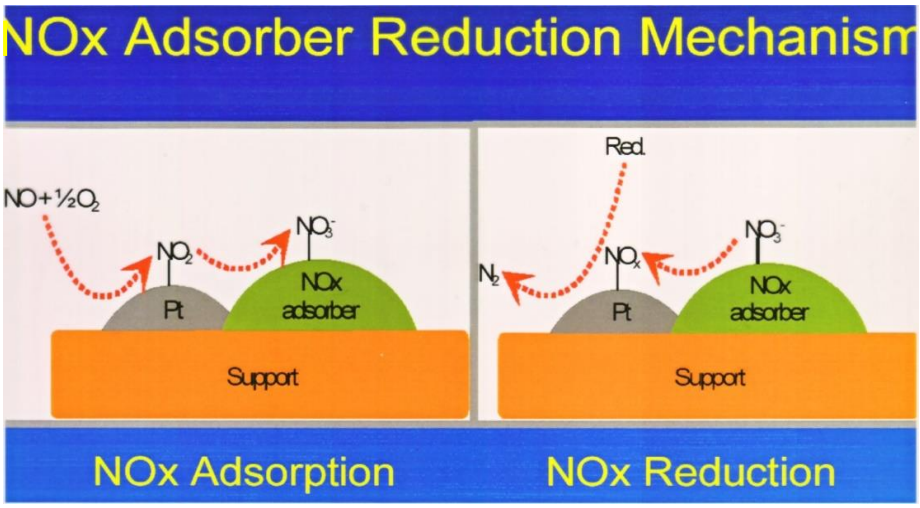

Fig 1. 3 NOx storage/reduction (NSR) mechanism representation [11]

During lean operation, NO is stored in storage material like barium carbonate, barium nitrate is formed and when the engine is operated in slight rich mixture for an instance (richer than ordinary operation), reduction reaction proceeds which releases NO, and this reduces the stored Nitrates to N_2. This cycle is also called NO_x storage and regeneration or lean-rich modulation. This conversion is very necessary to reduce the trapped amount of NO to N_2.

(a) $NO + ½\ O_2 \rightarrow NO_2$

(b) $BaCO_3 + 2NO_2 \rightarrow Ba\ (NO_3)_2$

(c) $Ba\ (NO_3)_2 \rightarrow Ba + N_2 + 3O_2$

The above equations and the *Figure 1.4* show the formation and reduction reaction of NO in Lean NO_x trap mechanism.

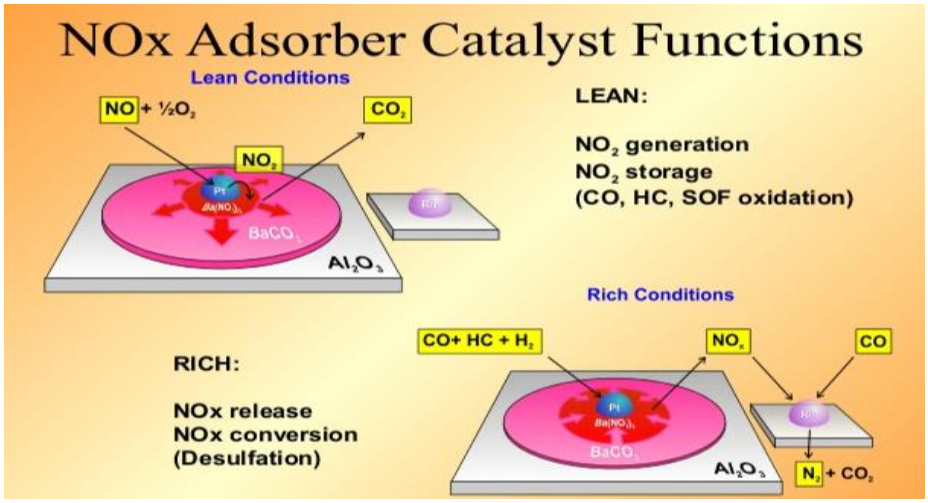

Fig 1. 4 Reactions performed in LNT [13].

1.1.4 Non-Selective catalytic Reduction (N-SCR)

N-SCR has both oxidation and reduction reactions performed in it. It is also called as three-way catalytic converter as it can perform two oxidation reaction and one reduction reaction in the presence of catalyst like Platinum. These reactions are more efficient only with rich combustion mixtures. During the initial phase of the reaction, CO and Hydrocarbons are oxidized to CO_2 and Water and in the final phase of the reaction, NO_x is reduced to Nitrogen.

$CO + O_2 \rightarrow CO_2$ (Oxidation)

$$HC + O_2 \rightarrow H_2O + CO_2 \text{ (Oxidation)}$$

$$NO_2 + CO \rightarrow N_2 + CO_2 \text{ (Reduction)}$$

1.1.5 Selective Catalytic Reduction (SCR)

SCR is one of the latest emission control technology by injecting water-urea solution in which urea is decomposed to form ammonia, in which the later reduces NO_x to nitrogen. This reducing agent is also called as Diesel Exhaust Fluid (DEF) [14]. Basically, to protect environment and our health, harmful pollutants (NO) are reduced by SCR to get N_2, and H_2O. Due to the strict legislation, SCR is widely used especially in Diesel Vehicles. As ammonia is dangerous to human health, DEF uses urea from the fuel station which is injected in to the exhaust gases which are flowing downstream from the engine to tail pipe are later hydrolyzed and decomposed to ammonia (NH_3) and this injected Ammonia converts the harmful exhaust gases to Nitrogen (N_2).

DEF is a non-toxic fluid containing Urea and water. This injection of fluid is called Ad-blue injection and it is called selective as its main target is to reduce the selected NO to N_2.

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \text{ (Standard)}$$

$$2NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O \text{ (Fast)}$$

$$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O \text{ (Slow)} \quad [16]$$

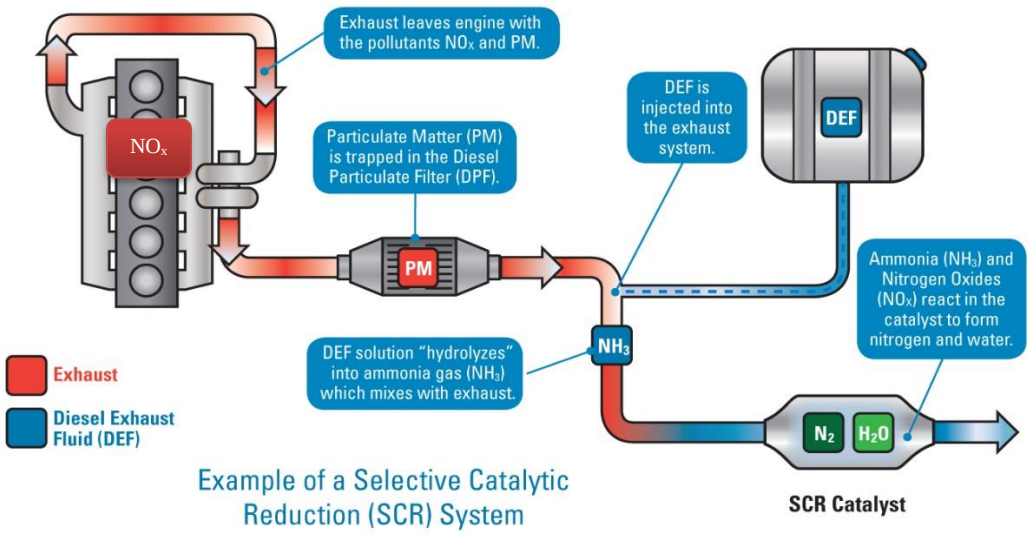

Fig 1. 5 SCR System and DPF in Diesel vehicles [15]

The above *figure 1.5* shows the system which is used to reduce harmful pollutants coming out from the tailpipe. The parts marked in red are harmful pollutants formed inside the engine cylinder which are exhausted. They are Particulate matter and NO_x which are harmful and they are converted to harmless substance with the help of trapping the particulate matters by DPF and conversion of NO_x to pure N_2 with the help of SCR system.

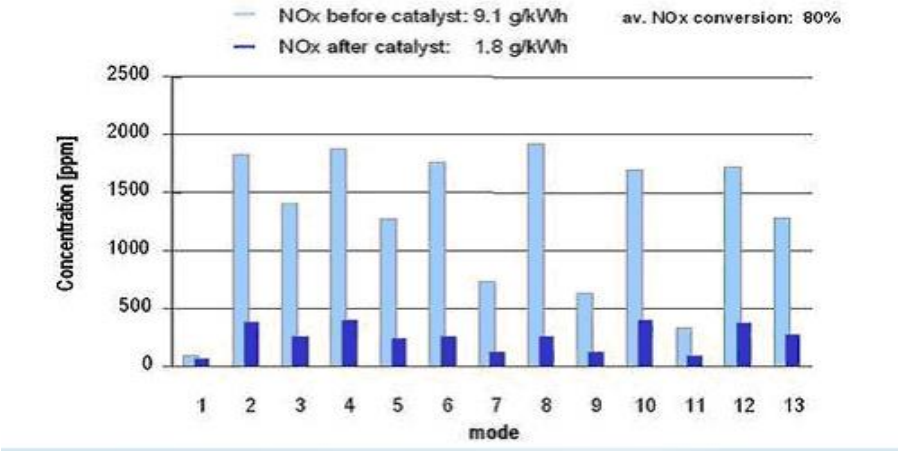

Fig 1. 6 Comparison of concentration of NO_x before and after catalyst [11]

The above-mentioned statistical graph in the *Figure 1.6* clearly shows the efficient performance of catalyst where the concentration of NO_x before catalyst was found to be enormously high when compared to the same after catalyst which clearly proves that it has a conversion efficiency of around 80 % as mentioned.

1.2 Effect of NO_x on Health and Environment

NO and NO_2 are poisonous irritant gases which affects human directly and indirectly. Direct effect of NO causes most of the trouble to human's respiratory system and cardio vascular system. There are around 72 thousand premature death annually in Europe (EU) due to excess NO_x when compared to traffic accidents which is responsible for killing only 39 thousand life [16]. At high temperatures, atomic nitrogen and oxygen molecules in the air combine to form Nitric oxide (NO) which is then oxidized to Nitrogen dioxide (NO_2). The production rate of NO_2 is faster when NO reacts with Ozone in the stratosphere or troposphere layer. These dioxides are toxic which damages the leaves of plants and slowdown the process of

photosynthesis in plants and can also causes irritation to lungs and some respiratory diseases especially to children and other living being [17].

Air pollution reduces human life expectancy by more than eight months on average and by more than two years in the most polluted cities and regions [18]. It also leads to abnormal coagulation of high concentrated fluid over the respiratory tissues. Excess Exposure to NO_x reacts with Vitamin B12 of human which causes some neurological diseases and reduction in Bone marrows [19]. Indirect problems due to NO_x are ozone layer depletion, Acid rain, Smog and poor visibility which indirectly affects human health. Excess NO_x destroys the stratosphere layer of Ozone which thereby increases the temperature of earth's atmosphere by direct exposure of high energy UV rays on the surface. Consequently, this results in change in climate, weather pattern, poor quality of air, and so on. Due to urbanization, increase of vehicles in the cities have led to serious pollution of air in which NO_x plays a major impact of ozone formation and aerosol in the atmosphere, acid deposition and radiation balancing. High Exposure to NO_x (2500 $\mu g/m^3$) for an hour decreases breathing capability of human which can lead to death, while exposure to ozone causes respiratory problems with additional symptoms like dry throat and headache [19].

Acid rain or Acid deposition is due to the storage of NO_x and SO_2 (Sulphur dioxide) on Earth's atmosphere from various sources like burning Hydrocarbon fuel powering vehicles, generating electric current in powerplants and oil refineries. According to United States Environmental Protection Agency, Electric power generation contribute one-fourth of NO_x present in the atmosphere. Acid rain damages Plants, soil, Monuments, Buildings and human health.

Photochemical reaction of sunlight with Hydrocarbons emissions and NO_x emissions from Automotive engines causes unwanted smoke and fog which is combined as smog. This creates problems of visibility on the road which causes major accidents and other problems to human which should be avoided completely. Due to visibility problems, government in many countries declares holidays for school and offices in order to reduce the risk of life and health [20]. Smog and invisibility have created severe issues in capital cities like Beijing (China), New Delhi (India), and London (United Kingdom) compared to many other countries. NO_2 absorbs full visible spectra of light which causes poor visibility [19].

1.2.1 Ambient Air Quality

Air pollution is one of the main causes for climate change, human health and environment. Air pollution kills at-least one in nine persons. They are mainly due to particulate matters and other harmful gases [21]. Also, air is the main source for any living organism to survive. This poor air quality causes breathing problems which destroys respiratory system of all living beings which also constitutes destruction of many animal species.

Many Governmental agencies and World Health Organisation (WHO) has set some standards and limits in order to protect human health by improving the quality of Air in the atmosphere.

The *Table 1.1* shows the concentration limit of Nitrogen Dioxide (NO_2) set by European Environment Agency considering Air Quality. More than 86% of NO_2 which is above the annual limit value were observed mostly in traffic signals. Traffic areas and congested street with vehicle are the major source of NO_x.

Pollutant	**Averaging period**	**Standard type and Concentration**	**Comments**
NO_2	1 hour	EU Limit: 200 μg/m^3	Not to be exceeded on more than 18 hours per year
	1 hour	EU Threshold:400 μg/m^3	Measured 3 consecutive hours over an entire zone.
NO_2	Calendar year	EU Limit: 40 μg/m^3	

Table 1.1 Air quality standards for the protection of human health from NO_2 [22]

The *Figure 1.7* shows the annual concentration of NO_2 in 2017 in European Union. Though the average annual European limit of NO_2 was 40 μg/m^3, from the figure it's very clear that most of the concentration of NO_2 are above the limit (last two red dots shown) in most of the European Country which means the legislation should be enforced to obey European limit as mentioned. Even Czech Republic which is in the central Europe in location has also high concentration of NO which is also proved by the experimental data and measurements done which is mentioned later in this work.

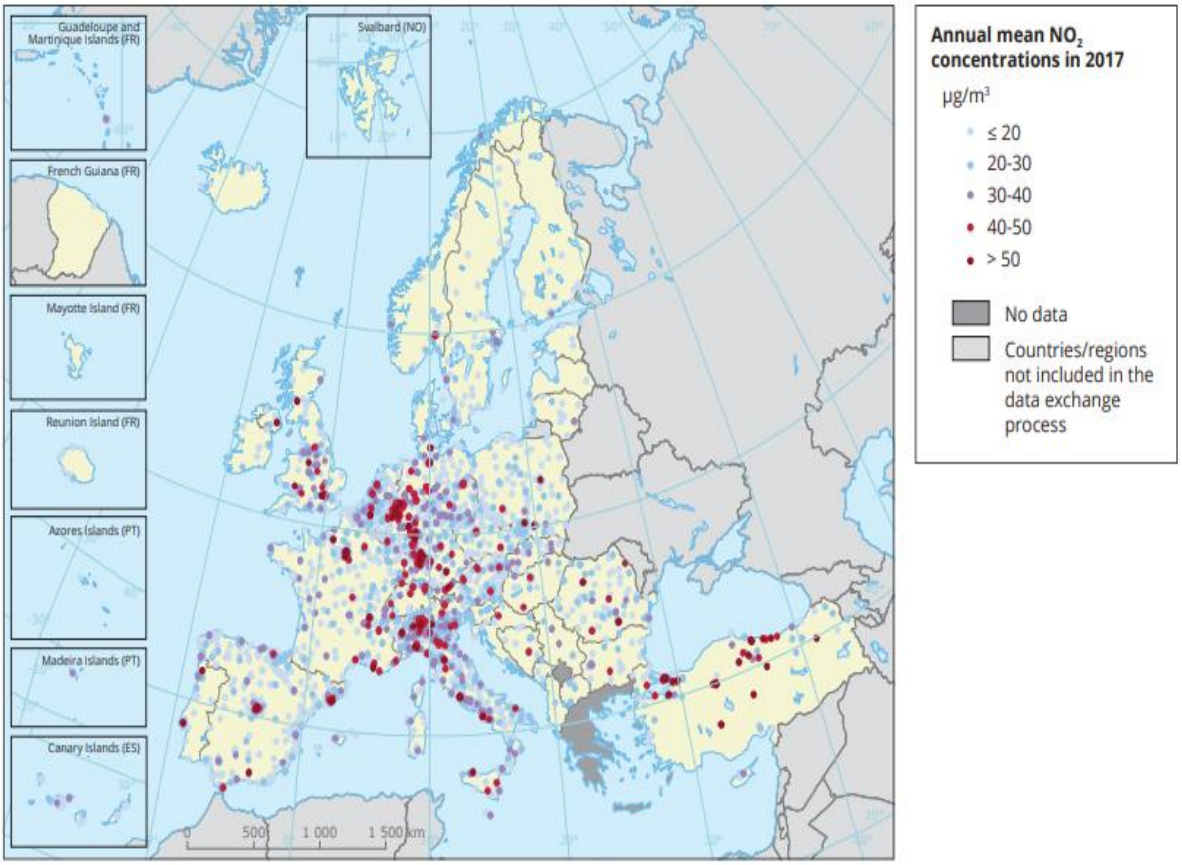

Fig 1. 7 Annual Concentration of NO_2 observed in different countries in 2017 [22].

1.2.2 Emission limits of Vehicles

As discussed above, exhaust emissions have a great impact on air pollution which has significant effect on human health and environment. Unless and otherwise if people are not educated or not aware of this issues, some strict rules or legislations should be enforced by the government. This lead to the segregation of Emission limits on vehicles based on their size, fuel and utility. Most of the countries have their strict vehicle emission standards- like European Union has Euro 6d currently which gives the concentration in parts per million (ppm) or grams per km (g/km) or grams per kWh (g/kWh).

1.2.3 European legislation for Heavy-Duty Vehicle Emissions

Nowadays, Vehicle manufactures are facing a very stringent guidelines on air pollution and their demand to meet European Emission Standards in considering the pollution level. The

following tables comprises the dates of implementation of Emission standards and new approved regulations for Heavy duty vehicles. EURO 6 regulations also provide additional information along with the tables 1.2 and 1.3 provided below [23];

1. Ammonia concentration limit to 10 ppm applies to both Compression Ignition and Positive Ignition Engine
2. A maximum limit to NO_x, especially NO_2 emission which may be defined at later stage.

Stage	Date	Test	CO	HC	**NO_x**	PM	PN	Smoke
			g/kWh				1/kWh	1/m
EURO I	1992, ≤ 85 kW	ECE R-49	4.5	1.1	**8.0**	0.612		
	1992, > 85 kW		4.5	1.1	**8.0**	0.36		
EURO II	1996.10		4.0	1.1	**7.0**	0.25		
	1998.10		4.0	1.1	**7.0**	0.15		
EURO III	1999.10 EEV only	ESC & ELR	1.5	0.25	**2.0**	0.02		0.15
	2000.10		2.1	0.66	**5.0**	0.10		0.8
EURO IV	2005.10		1.5	0.46	**3.5**	0.02		0.5
EURO V	2008.10		1.5	0.46	**2.0**	0.02		0.5
EURO VI	2013.01	WHSC	1.5	0.13	**0.40**	0.01	8.0×10^{11}	

Table 1.2 Emission Standards for Heavy Duty Diesel Engines – Steady state Testing [23]

Stage	Date	Test	CO	CH_4[a]	**NO_x**	PM[b]	PN[e]
			g/kWh				1/kWh
EURO III	1999.10 EEV only	ETC	3.0	0.65	**2.0**	0.02	
	2000.10		5.45	1.6	**5.0**	0.16[c]	
EURO IV	2005.10		4.0	1.1	**3.5**	0.03	
EURO V	2008.10		4.0	1.1	**2.0**	0.03	
EURO VI	2013.01	WHTC	4.0	0.5	**0.46**	0.01	6.0×10^{11}

Table 1.3 Emission Standards for Heavy Duty Diesel Engines–Transient state Testing [23]

Emission limits are set for type approval tests to improve the air quality. So conformity factor is introduced to compare the emission limits. Conformity factor is the ratio of Real drive emission measured to the set emission limits measured in testbench.

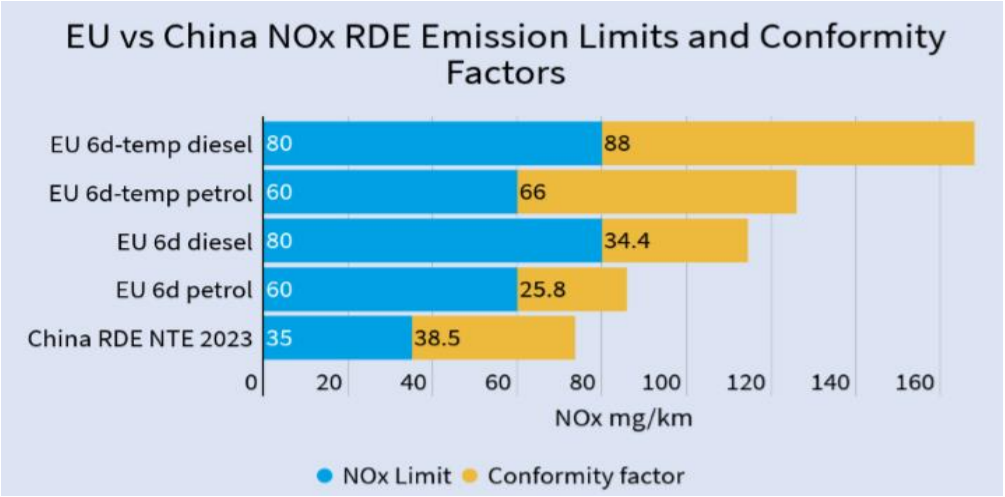

Fig 1. 8 Comparison of concentration of NO_x in China and Europe with RDE limits and Conformity factors [24]

Conformity factor is not to Exceed limit which shows that Real drive emissions is quite higher than set limits because of various barriers like climatic condition, traffic signals, fuel quality and Air quality. Bringing conformity factor to 1 means, RDE and Set limits are same, which is very ideal to achieve.

Considering the air quality, China, European and other countries are trying to achieve or control the excess NO_x emissions from the automotive and other industrial sector.

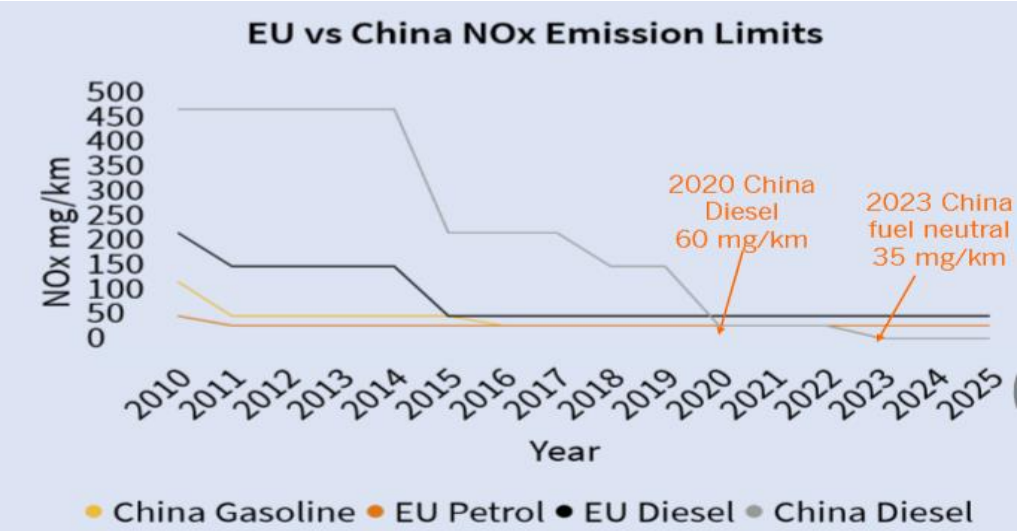

Fig 1. 9 Comparison of Emission limits of NO_x in China and Europe [24]

The above *Figure 1.9* clearly shows how the strict regulations and government legislations have played a major role in reducing the exhaust NO_x emissions from the vehicles in the last decade. This is done in order to improve the quality of air.

1.3 Excess Emitters

To increase the performance, increase the fuel economy, decrease the operation cost and to eliminate the repair cost, tampering of some Emission control systems is done by some manufacturers or vehicle owners by using emulators or other tampering devices which are available in the market [25]. Some tampering or zapping methods are described as follows:

EGR can be tampered Mechanically and by external zapping device. Mechanical Tampering are done by some physical changes like sealing the hose to vacuum actuator and blocking the recirculating gas tube in engine compartment. External zapping device are done by installing an external black box plugged behind EOBD socket [25].

SCR can be tampered by disconnecting the circuit and emulating its function to the ECU, removing the fuse from SCR system, showing Ad-blue tank gauge some constant value independent of reality and Reagent tank level doesn't display the exact gauge level in Dashboard. DPF can also be removed and can be tampered by emulating its function to the ECU [25].

These tampering devices are available in markets and can be purchased through online or in stores and can be installed by Mechanic or technician. These tampering can be avoided or made difficult by making some anti tuning control unit which would register all the activities performed and it can be read, but not manipulated [25].

Such high emitting vehicles are the major source of environmental pollution and causes of problems to human health which enforced strict legislation by the government. This should be strictly followed and periodically inspected in order to avoid manipulation.

1.4 Detection of Excess Emitters

The major harmful emissions from the Engine Exhausts are Oxides of Nitrogen (NO_x), Particulate Matter (PM), Carbon monoxide (CO) and Hydrocarbons (HC). Heavy-duty diesel vehicles on on-road emits quite a lot of NO_x and particulate matter. Such on road emissions can be detected by **in situ** method - tunnels, parking areas and remote sensing studies and by **in vehicle** - probe vehicle and car chase studies [26]. Emissions from heavy-Duty diesel trucks, especially high emitters can be detected in various methods like chassis dynamometers, in a tunnel, on the road side, remote sensing or vehicle chase method. Chassis dynamometers is one of the most commonly used method for measuring emissions and other characteristics of vehicle in factory and in laboratory. But the emissions measured by this method can be different from real drive emission measurements. Though they are controlled and measured by changing different parameters, but the environmental and operating condition is not the same [27]. Tunnel measurement is one of the other methods to measure the emissions during real drive where the pollutants would be high in traffics in which vehicle speed and their corresponding emissions are measured by collecting the plumes [28]. Remote sensing is one of the other effective method which is used to detect the excess emissions by detectors, which is a light source (UV or IR). The main disadvantage in this method is that the calibration gas is taken along with in order to compare the gases with minimum concentration [29] in order to get the exact concentration by differentiating background. Road side measurement is similar to remote sensing method where the sampling lines are placed at the corner of the road or at some traffic places where good measurements can be recorded from the running or on going vehicles [30]. Vehicle chase method is also another emission measurement technique in which the measuring instruments are loaded in a van/vehicle. The

main difference between road side measurement and vehicle chase method is in the former, sampling line is stationary on the side of the road where the measurement is happening and this records the exhaust plumes of the moving vehicle and their vehicle details are noted with the time whereas the latter has the measuring instruments loaded in the vehicle and the tested/measured vehicles are recorded. So, in vehicle chase method, both the instruments carrying vehicle and the targeted vehicle are moving, except in the place of heavy traffic.

This work is concerned mainly to detect excess NO_x emissions by a chase vehicle where heavy duty diesel trucks were targeted and followed over a time period and elevated concentration were inferred during the measurement. The limits of NO_x have exceeded as defined in the Air Quality directives especially in densely populated metropolitan areas. In real drive, NO_x emissions from Diesel vehicles have exceeded the limits leading to homologation [31].

In a pilot study conducted in vicinity of Prague, the exhaust plumes of heavy-duty diesel vehicles were detected and analyzed by a chase vehicle equipped with a fast response gas analyzer. The main goal of this project is to analyze the data collected from the heavy-duty trucks near *Benešov* (Prague - Brno Highway) and verify the effective performance of newer NO_x after treatment device. One of the most problematic pollutant in Europe and in many other countries is NO_x, which has a very negative impact on health and environment. The maximum allowed annual limit of NO emissions in most European cities is $40 \mu g/m^3$ [32].

Such emissions are due to tampering or emulators of Selective Catalytic Reduction (SCR) and manipulation of some other after treatment devices in vehicles or from the exhaust of other industrial source or burning of harmful substances that pollutes air. But nowadays, due to strict government legislations and European standard regulations, Vehicle manufacturers are in a tight situation to achieve these low Emissions with complicated after treatment systems and technologies. These vehicles meet and obeys the legislations before it comes to the market, but they are not meeting the standards in Real Drive. Considering the emissions from vehicles, Real Drive emissions (RDE) are quite higher than the current Euro Normal Standards. But this is due to the fact that RDE is rarely and randomly investigated [32] which should be frequently checked and followed in order to meet the current standards and reduce the pollution which thereby reduces the impacts on human health and environment.

2 Goal of the Thesis

The main goal of the thesis is to detect excess emissson of oxides of Nitrogen (NO_x) in real drive and to analyze the measured data from Heavy duty vehicles travelling on the D1 Motorway, in the vicnity of Prague, by using vehicle chase method. The various tasks performed during the experimental campaign are

a) To participate in the part of the experimental campaign to conduct the experimental measurement.

b) To follow/chase some heavy duty vehicles and measure their emission of NO in both directions of Prague-Brno D1 Highway with the help of fast response FT-IR Gas Analyzer.

c) Analysis of measured data which represents NO concentration through some basic statistical approach and evaluation of detection limits in order to calculate the ratio of NO/CO_2.

d) To calculate the NO/CO_2 ratio by Numerical integration of the Peak Area, Ratio of Maximum point of concentration and Linear Regression approach and find the consistency between these approaches.

e) To compare NO/CO_2 between these approaches and evaluate the Emission factor from the analysed data and judge on the performance of SCR.

3 Experimental Setup

3.1 Vehicle chase Method

The most important and interested vehicles focused in this study are heavy duty vehicles. In order to find the excess emitting heavy duty vehicles, vehicle chase method was used. This experimental measurement was conducted for a week near a small city named Benešov, in the vicinity of Prague. On 03.06.2019 morning, the measuring instruments were installed and set up in the Customs administration van of Celní správa. The measurements were done for a week from 03.06.2019 afternoon to 07.06.2019 which concluded with useful data from about 230 heavy duty vehicles. The sampling site selected was Prague – Brno highway, so that the emissions can be measured for individual vehicle over a time period by avoiding possible disturbance and traffics due to vehicles, whereas disturbances like wind and cluster of vehicles going at the same time is uncertain and questionable to avoid, which makes hard to predict the exact measurements from the exact vehicle as the plumes gets mixed with the other.

This vehicle chase method is better and efficient than road side stationary measurement by connecting sampling lines to measure exhaust plume near road side or in bus station [30] or some measurements done near entrance to tunnel. The instruments were installed in the Customs administration van to conduct measurements and the sampling pipe was projected in-front of the van so that this would be able to collect the exhaust plumes from the vehicles going in front and give the measurements and concentrations through the computers installed along with FT-IR and the results were reviewed. These instruments also need power supply to ensure that they operate continuously and so power is taken from the transporting vehicle and/or additional batteries.

During this field measurement and study, registration number of vehicles and the time of chasing individual vehicles were noted with reference to the time shown by the instruments and computer connected with the instrument which displays the output concentration. This helped to quantify the difference of time between consecutive or different vehicles.

Also, technical data comprising of vehicle details, model and European standards or regulation of the vehicle were collected from toll system. The vehicle used for the measurement campaign, instruments and the sampling lines installed in the vehicle are shown in the following figures.

Fig 3. 1 Customs administration vehicle used for vehicle chase method.

Fig 3.2 Sampling line installed to collect exhaust Plumes from the vehicles

3.2 Instrument used for the Measurement

There are many experimental instruments used to measure individual concentration of gases and are calibrated according to the manufacturers and the requirements. Some of the instruments that measures the concentration of NO_x are Chemiluminescence, Non-Dispersive Infra-Red Analyzer (NDIR), Fourier Transform Infra-Red Spectroscopy (FTIR) and so on. In this study, FTIR instrument with a fast response gas analyzer is used to measure concentration of NO and CO_2. Though there are many other gaseous pollutants, this study is focussed only on the measurement of NO in comparison with CO_2. As the basic product of complete combustion of fuel is CO_2, the emission factor for NO can be derived with respect to the concentration of CO_2.

3.2.1 Fourier Transform Infra-Red Spectroscopy (FT-IR)

Fourier Transform Infra-Red Spectroscopy works on the basic principle that individual Gas absorbs light. The IR spectra is obtained by Fourier Transform of light intensity of superposition of two light beams of varying path length, passing through an optical cell with sampled gas.

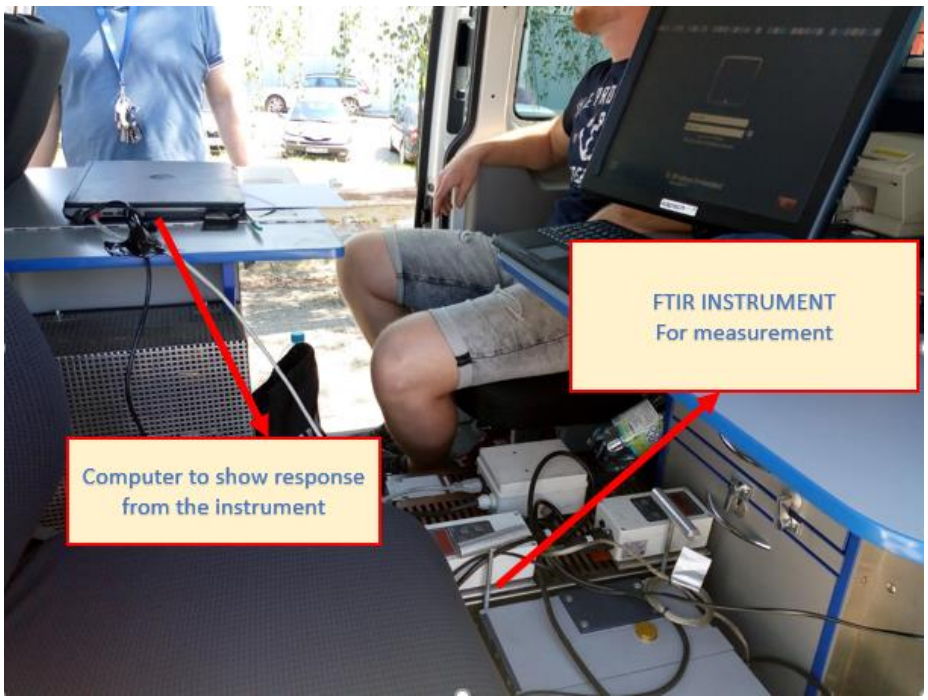

Fig 3.3 Instruments installed in Customs administration vehicle

FTIR is used to identify organic and inorganic chemical compounds with their bond structure by the absorption of Infra-red spectra. Every molecular bond vibrates in their own/or different frequency and this absorption of light energy causes the molecules to move to excited state from the initial state. The wavelength of light absorbed by the sample gives the molecular structure which is the energy difference between the lower (initial) state and the excited (final) state [33].

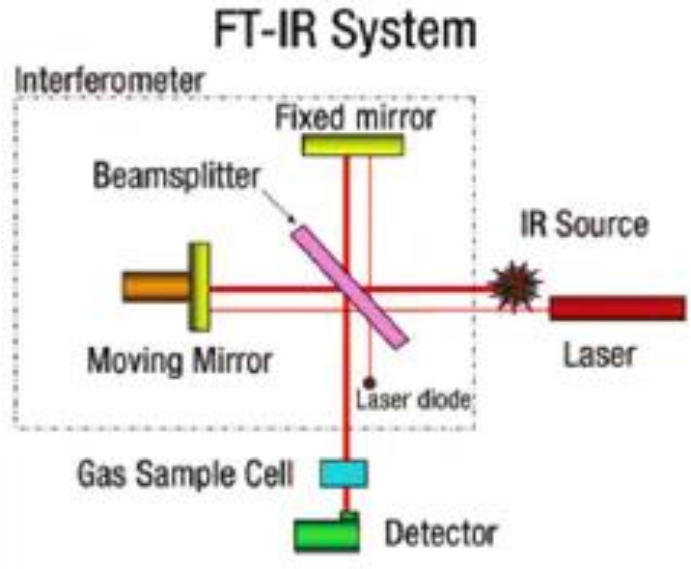

Fig 3.4 FTIR – Working Principle [33]

The FT-IR instrument used for sampling the exhaust emissions in our experimental study is Automated Fast response Gas Analyzer from Bruker brand which is Matrix MG Series model. It is a very high-performance compact analyzer which is designed for high precision, automated and real-time monitoring of gas concentrations in various applications. It is enclosed with OPUS GA software which evaluates the spectra in real time for identifying the concentration of gaseous compounds. This type of instrument is used in wide variety of applications like food industry, process surveillance in production lines, exhaust gas monitoring from smokestacks, Bio gas and motor vehicle analysis and in other scientific research [34].

Figure 3.5 shows the instrument used in our experimental campaign for real drive emission measurement by Vehicle Chase studies.

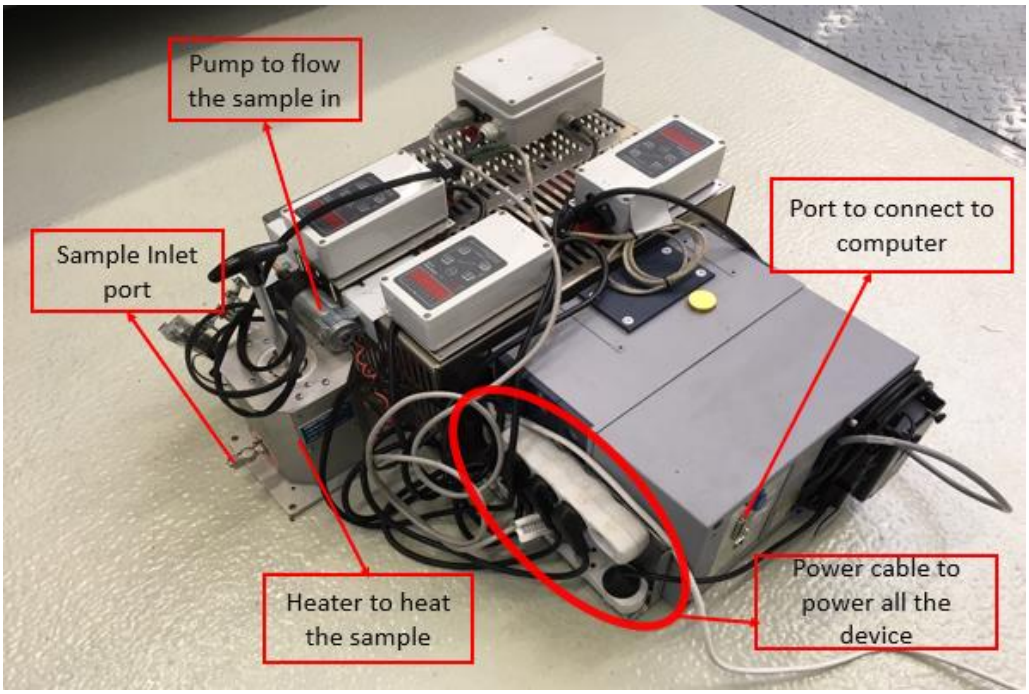

Fig 3.5 FTIR used for Experimental Measurement

The cut section of the instrument is shown in the *figure 3.6* which is fast response and high-performance gas analyzer.

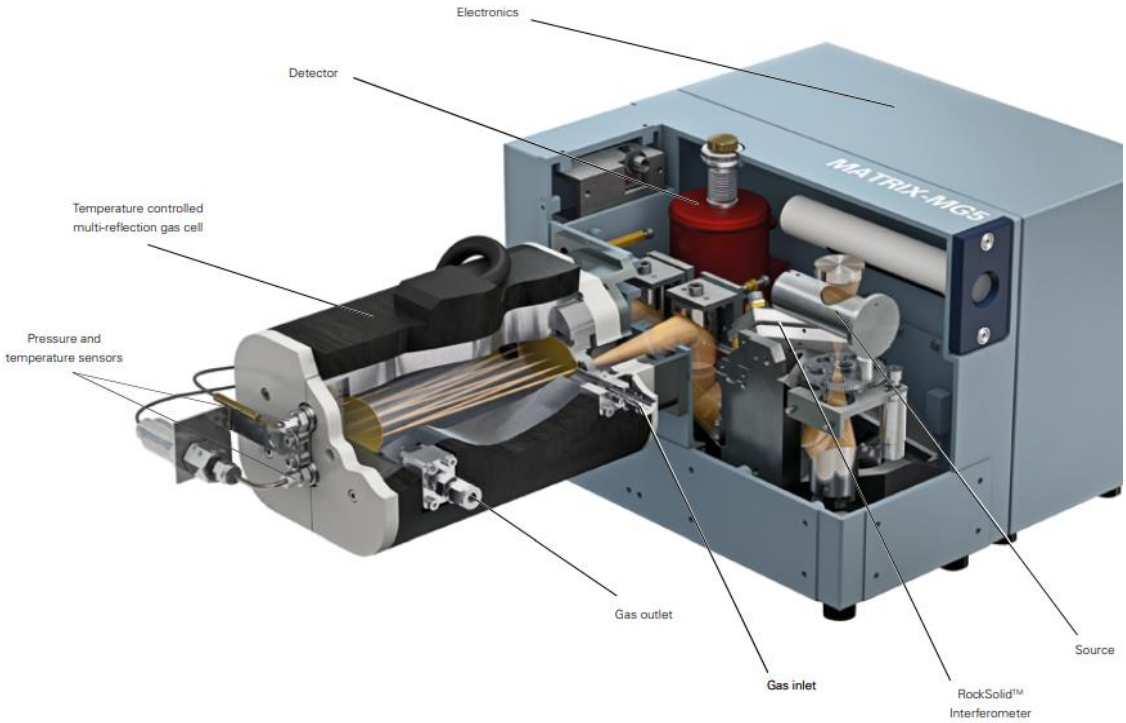

Fig 3.6 FTIR – Matrix MG5 Series Cut Section [34].

3.2.2 Instrument specification

The concentration of gaseous pollutants in the exhaust were obtained from infra-red absorption spectra taken by FTIR spectrometer Bruker MGX (MCT detector cooled by liquid nitrogen, ZnSe optics, 5m optical cell path length, 0.5 per cm of resolution, 5 Hz) and analyzed using software Opus GA (Bruker, Germany) for concentrations of NO and CO_2. The FTIR spectrometer together with spectra deconvolution methods were calibrated throughout the concentration ranges expected in raw vehicle exhaust using span calibration gases and a gas divider for CO_2, CO, NO, NO_2 and other gases [35]. The calibration of the FTIR analyzer for low concentrations of NO and CO_2 and its validation for on-road measurement of NO/CO_2 ratio is an ongoing effort.

Fig 3.7 Team involved and vehicle with the instruments installed for the measurement

The above *figure 3.7* shows the team helped in installing the instrument setup for the measurements to happen. FT-IR is installed in between the rear seats of the van and the sampling tube in extended through the front cabin to outside to collect the sample of exhaust gases and the measurement data were recorded.

4 Data Analysis Procedure

As mentioned before, experimental measurements were performed, and the obtained measured data were further analyzed to get a valuable information. The FT-IR instrument used in this measurement is used to identify the concentration of NO and CO_2 especially from the exhaust gases of the combustion engine. This instrument has a very high time and spectral resolution and it's very quick to respond which avoids/reduces the time shift between the measurements and the response. The main aim is to calculate the ratio of NO to CO_2 based on the recorded readings. In order to proceed for further analysis, feasible steps are carried over to calculate the emission factor and find the high emitters.

4.1 Instrument response to Concentration – Signal and Noise

The beneficial information is obtained from the physical quantities like signals over a period when the samples are collected from the exhaust emissions or plumes of the vehicle. Some disturbances in signals are referred as Noise, which are due to vibration of the instrument, electrical phenomena and other factors which disturbs the useful response of the instrument and are superimposed on the measurement. Generally, noises are either external or internal [36]. Internal noises are associated with components itself and external noises are due to vibration or other effects that distract or disturb the instrument.

Signals obtained from the sample includes noises which should be avoided as they are not the useful response representing the emission concentration. These can be eradicated either by subtracting the output response obtained from the sample to the background response obtained before exposed to the sample or by creating a base line from the spectrum obtained and differentiate the signals below the baseline which are commonly referred as noises.

Strength of the signals can be calculated by signal to noise ratio, which compares signals with noises to distinguish the background noise from the useful signal which is detected by the detector.

Signal to Noise Ratio (SNR) = Signal mean (μ) / Standard deviation of the noises (σ)

Mean of the signal (μ) is the useful signal of the sample excluding the noises and the Standard deviation (σ) of the noise is the signal obtained on the blank which were calculated by excluding the signals [30]. The FTIR has a fast response output as the controlled flow avoids turbulence disturbances and gives more precise signal according to the concentration of sample [34]. The instruments response obtained during the measurement is plotted with respect to time and the next process is to distinguish the unwanted noise from the response obtained.

4.2 Baseline and Peak identification

The desired method to quantify peaks are baseline correction, finding the peak area and visualization of detection of concentration which would reduce a considerable amount of uncertainty in the measurements and analysis. Initially, Baseline is mainly plotted on the areas where there are no peaks and the baseline in the area of the peak is calculated by linear interpolation between short areas before and after peaks or they can also be obtained by linear regression methods which surrounds nearby points [37].

The method used in this study to differentiate unwanted signals is to create a baseline for the response obtained by subtracting 20^{th} percentile of the response as represented in the following graph. Subtracting the created baseline from the instrument response gives the net concentration.

In the following graph in *Figure 4.1,* concentration of NO_x is plotted over a period which was obtained from the on-road measurement done on the first day of measurement. It's very clear that blue signals are the response obtained from the measurement, but they have a shift in concentration measured and so baseline was taken. A 20^{th} percentile was considered as the baseline for the background signal. The pink line denoted in *Figure 4.1* shows the 20^{th} percentile in which the signals or response below these are considered as noise. Subtraction of these two graphs (Blue and Pink) gives a net measurement (Black).

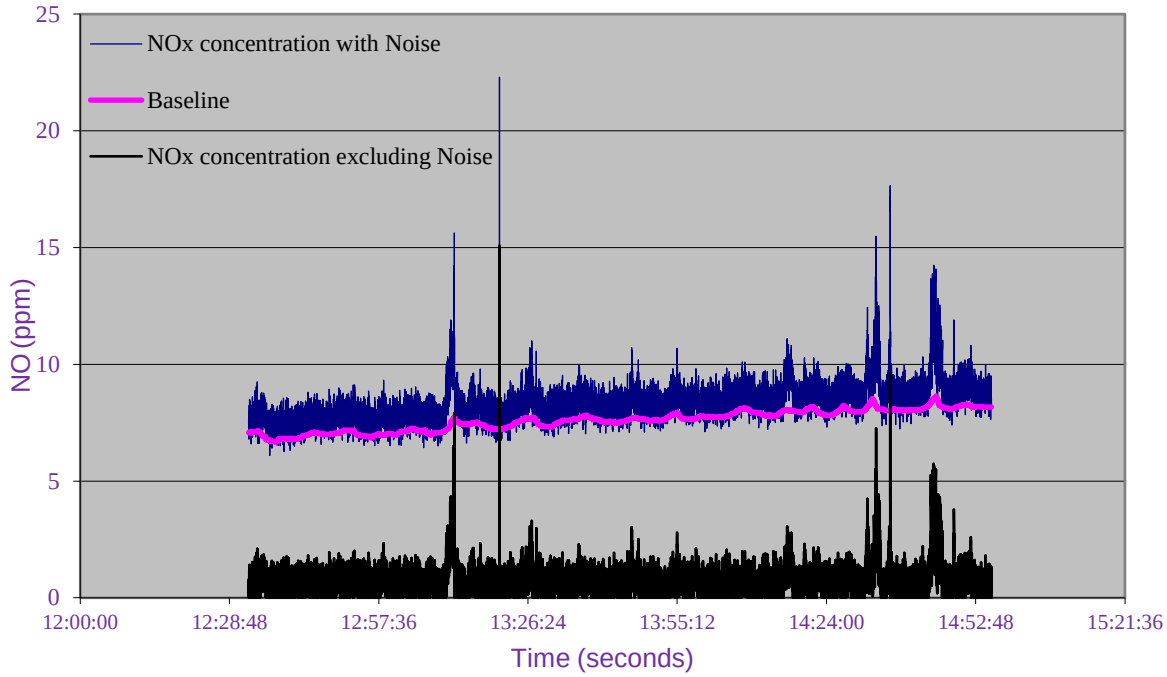

Fig 4. 1 NO_x concentration over the time period measured on 3rd June 2019 – Afternoon

The concentration of CO_2 is also plotted over the same period, applying the same subtraction of 20th percentile of measured concentration as a background.

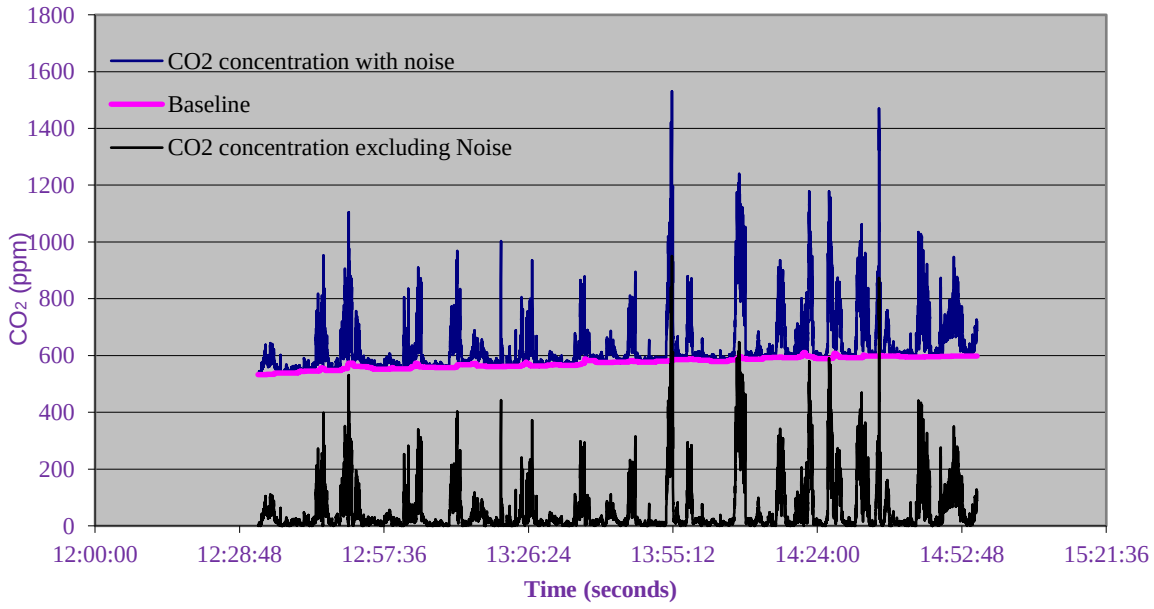

Fig 4. 2 CO_2 concentration over the time period measured on 3rd June 2019 - Afternoon

4.3 Detection limit in this setup

Detection limit is the minimum concentration of the sample detected by the instrument which can be clearly differentiated from noise. Detection limit may not be the same as provided by the manufacturers specification as it varies with time when they are exposed to different environmental conditions, different location and different operating condition. There are two types of Detection limit, namely

- Instrument Detection Limit (IDL)
- Method Detection Limit (MDL) [38].

4.3.1 Instrument Detection Limit (IDL)

In IDL, there are some signals obtained when the blank is analysed without exposure to the sample, these are referred as background signals or noises. These noises fluctuate around the background and so standard deviation of the background signal is calculated in order to set the detection limit to detect the useful response of the instrument which can be distinguished from the noise up to a certain level of confidence limit in statistical approach [38].

4.3.2 Method Detection Limit (MDL)

In MDL, there are some signals obtained from complex compounds which may be not necessary for the current measurement. These signals may be also due to the presence of some concentrated compounds which can show error in the response obtained [38]. These errors may also increase the measured detection limit and so this must be detected and set accordingly with signal to noise ratio as an approximate estimation.

The measurement was done on a moving vehicle and so this environment where the experiments happened was different and so, two types of errors are considered generally to set the detection limit. They are Type I error which detects something that is not present (probability of false positive) and Type II error which does not detect anything, though something is present (probability of false negative) [39]. These errors are considered as there are a lot of uncertainty in the measurement.

Detection limit can be given as [39],

$$\text{Limit of detection} = \text{LOD} = \text{SD} * 3.3$$

Where, SD is the standard deviation of the sample without concentration. Generally, there are matrix of concentration of various compounds in the atmosphere and so the standard deviation (SD) of the response obtained in the background signal without any response or exposure to vehicle emission helps to evaluate the detection limit.

Initially, standard deviation of response before sampling is calculated and then they are multiplied with 3.3 to get the detection limit. This detection limit is the minimum limit where the instruments response above this limit gives the useful concentration from the measurement.

4.4 Time synchronization - Vehicle and Measurements

The technique synchronization employed to match the timings of the recorded vehicles and the response obtained from the measurement data after analysis. The time recorded by the instrument, the computer used for showing the output signal and the standard time which we follow on regular basis were the same and so during the vehicle chase study, the vehicles whichever chased/followed were noted down along with the timing manually so that it would help to compare with the analysis of data and this matching would enable us to find the high emitting trucks.

The vehicle details, especially the heavy-duty vehicles registration number were noted down and the corresponding time of following/chasing the truck was also noted down for better correlation and comparison of data after analysis which would synchronise the measurement. As the measuring instrument used in this vehicle chase study was very sensitive and fast response gas analyser, drift in response time was avoided completely which is an advantage to get more accurate results.

The instrument was turned on for the measurements and the corresponding signals were recorded from the start and it was saved with the file name representing corresponding dates and time. These data were used for further analysis and later, they are synchronised with the corresponding vehicles.

4.5 Emission Factor

NO/CO_2 ratio is an important term which is essential to figure out the amount of pollutant released to the atmosphere to the amount of fuel consumed in which all carbon in the consumed fuel is assumed to be oxidised to carbon dioxide (CO_2) which is very hard to achieve it 100 % in practical case as all fuels are not burnt completely. Though all the carbon from the hydrocarbon fuels are not oxidised to CO_2, some are chemically decomposed to carbon monoxide (CO). So real emission factor should be the ratio of oxides of nitrogen to the summation of carbon monoxide (CO), CO_2, HC and PM. But in diesel engines, concentration of CO is negligible compared to other gases. But this ideal case is assumed to be achievable and emission factor is formulated as follows [40]. In this experiment, emission ratio is defined as the ratio of amount of NO_x to the amount of CO_2.

$$\text{Real Emission ratio} = [NO_x] / \sum ([CO_2] + [CO])$$

$$\text{Assumed Emission ratio} = \text{Concentration of } [NO] / \text{Concentration of } [CO_2]$$

In this study, NO/CO_2 ratio was calculated from the data by correlating the signals obtained from the concentration of NO to the concentration of CO_2 over a period either by linear regression approach or by peak area approach where the full portion of the peak is considered and their ratio is calculated or maximum values within a peak area is considered and their ratio is calculated. All these approaches were taken in to account for the measurement data and these approaches were compared and checked for consistency.

5 Approaches to calculate NO/CO_2 concentration

In this work, NO/CO_2 ratios can be evaluated by calculating the area of the peaks through numerical integration over the regime and their ratio is considered, by taking the ratio of maximum concentrations within the peak, or by linear regression approach. Based on this approaches, high emitters, low emitters, and inconsistent emitters are noticed.

5.1 Selection of peak reasonable area

As discussed in the previous chapter, the obtained signals are plotted with respect to time and the baseline is created to exclude noise from the measured response. After creating baseline, detection limit is calculated as per the formula discussed in the previous chapter which is 3.3 times the standard deviation of the baseline correction. This detection limit is the threshold limit in which the signals obtained above these are the useful response in which the instruments measures. As the main target is to calculate excess NO emitters with respect to the dependent desired combustion product (CO_2). So, the peak CO_2 corresponds to the chased trucks and NO produced during these periods are considered and analyzed. As this makes sense, that NO is produced from the vehicle and so corresponding emissions are measured with an exception that surrounding vehicles can disturb the exact vehicle's response. So, other vehicles should be also looked during the test.

The *Figure 5.1* shows only peaks of concentration of CO_2. Peaks, defined as areas which are above the detection limit, are considered for further analysis. The green circle shows areas which are above the detection limit are used for analysis to show in this work as an example in *Figure 5.3*.

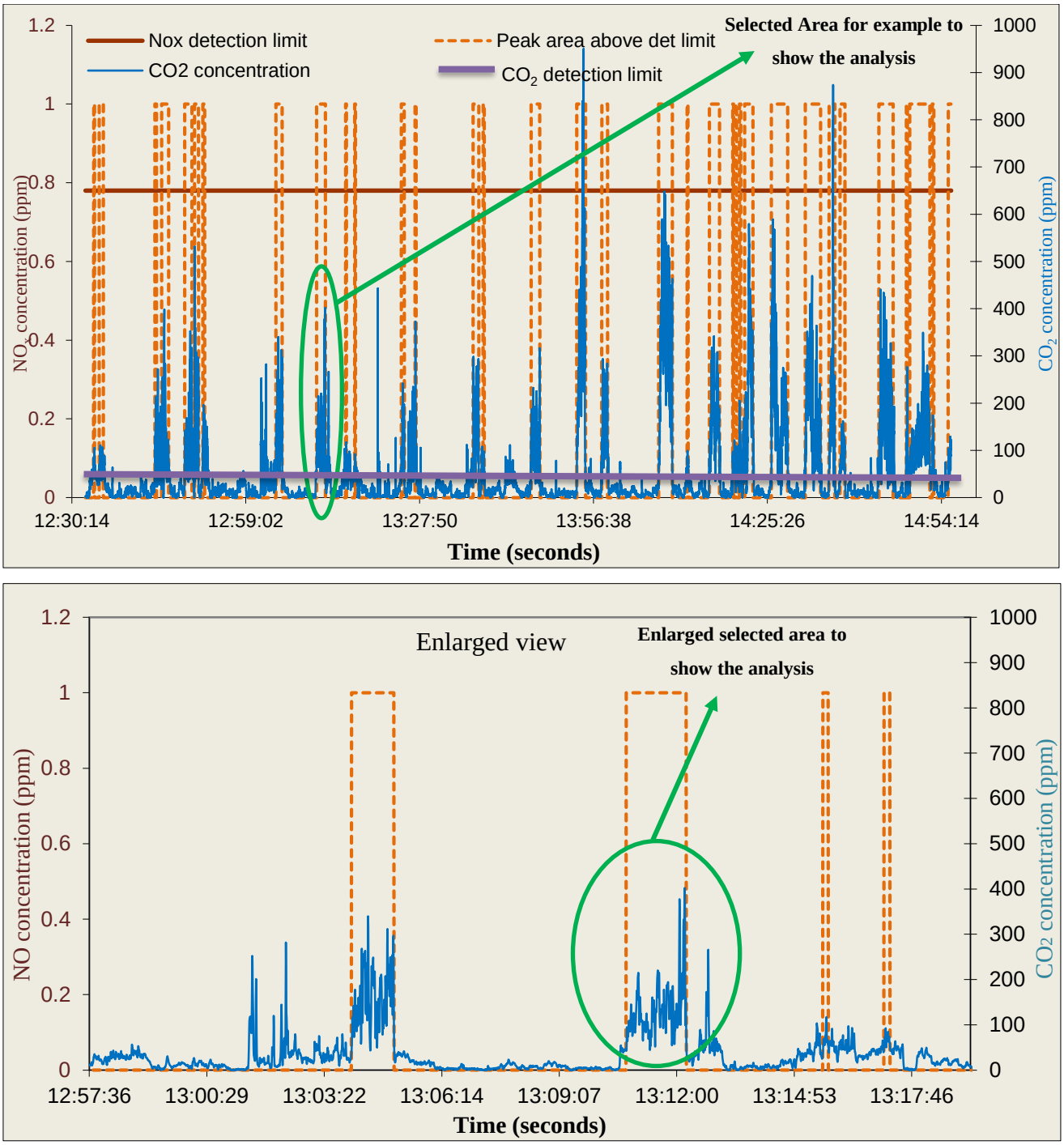

Fig 5. 1 Analysis by considering only peak areas which are above detection limit

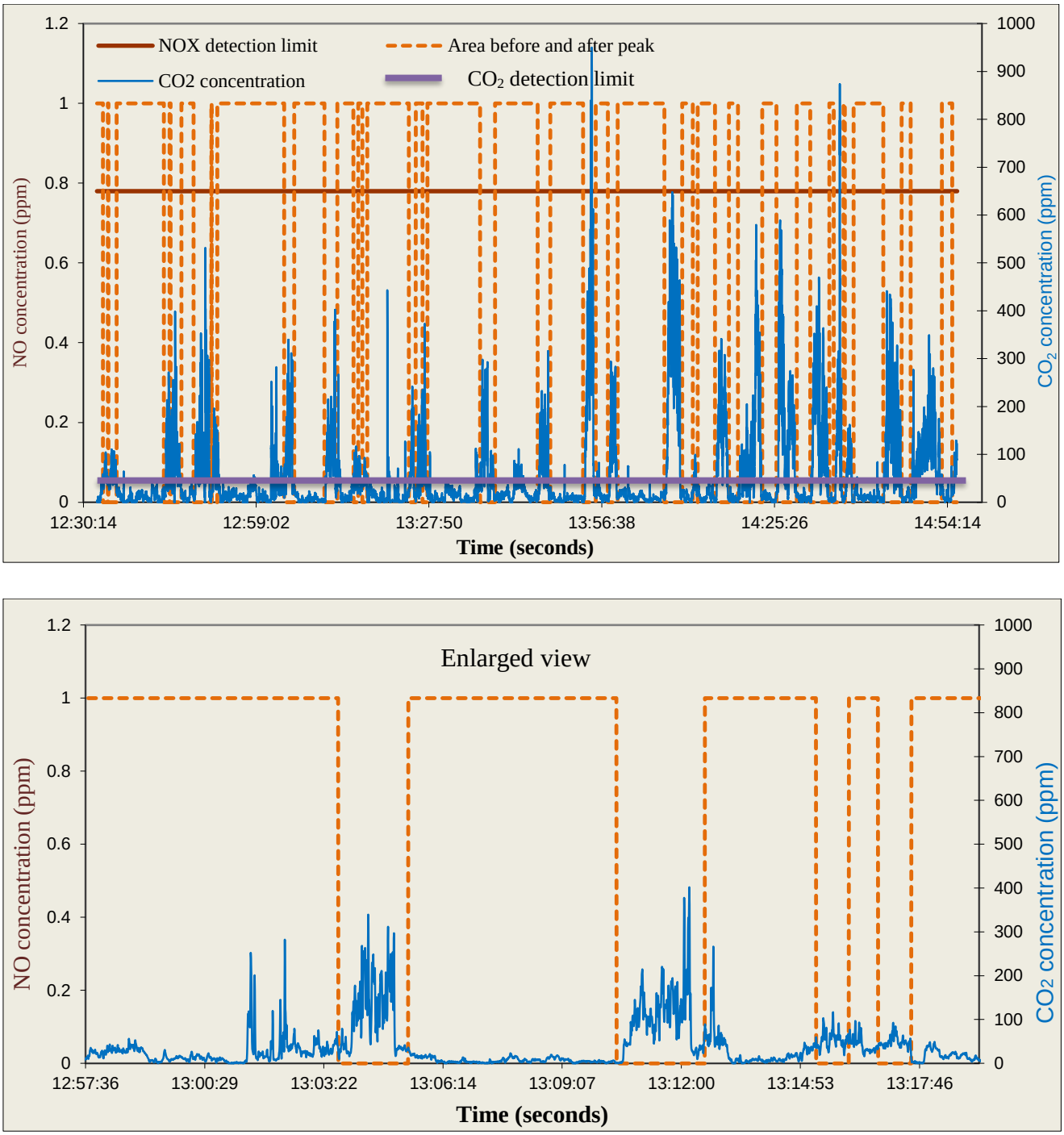

Fig 5. 2 Selection of areas before and after peak which are below detection limit

Figure 5.2 is similar to the previous representation which shows only the concentration of CO_2 in *Figure 5.1*, but the only difference in this figure is that the area which are below the detection limit were differentiated to separate from the peak which is a reasonable estimation to work only with the useful peaks for analysis and evaluation.

5.2 Peak Area approach

Peak area approach is one of the methods which is used to find the useful peak area that corresponds to the excess concentration obtained in the output response of the instrument after measurement. These areas formed by the concentration curve are calculated by integrating over the region formed by selecting the entire points which corresponds to the peak curve that are above the detection limit. Later the curve formed by the points are subtracted from the baseline in order to get the effective area of the peak by differentiating the background or the unwanted noises.

After numerical integration over the effective regime, the ratio of area of NO to the area of CO_2 was calculated in order to find the emission ratio. As there was some disturbance or many events of signal obtained during the response of the peak concentration, Area of the peaks were divided into few intervals. In this approach, concentration of NO and concentration of CO_2 were plotted separately, and they are integrated over the time period by selecting the points and the background is subtracted to get the useful area of the corresponding concentration. Later, both the areas of concentration of NO and CO_2 are divided to get the corresponding Emission factor or Emission ratio. The below *figure 5.3* shows the enlarged section of selected area from the *figure 5.1* which are shown as an example with multiple events performed in the same vehicle.

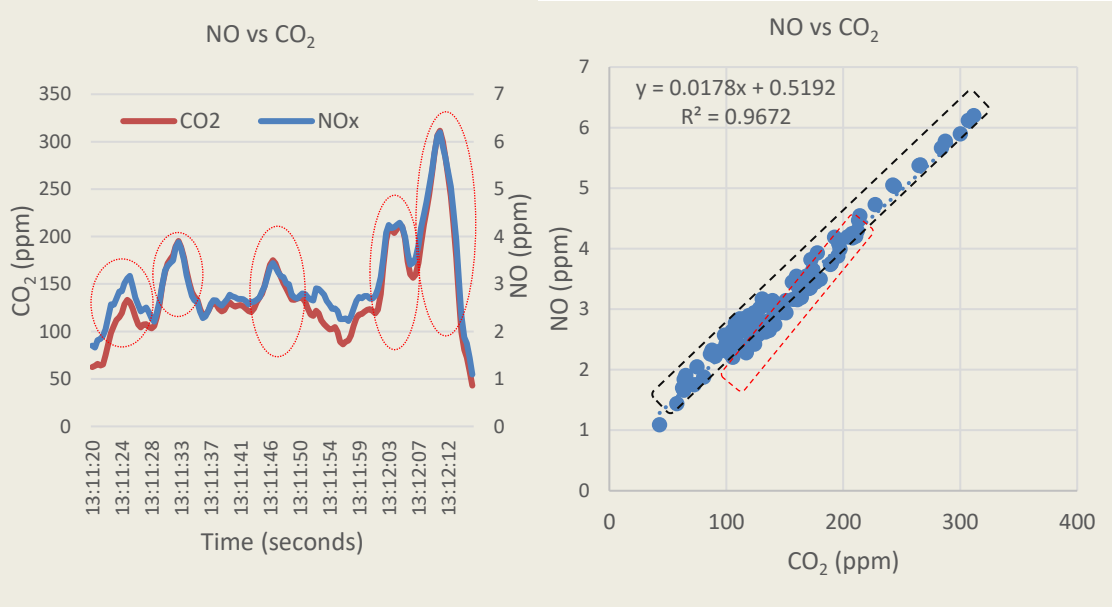

Fig 5. 3 Example considered for finding the area from the measurement on 3rd of June

The above *Figure 5.3* shows the concentration measured from a truck with vehicle number *BH3XXXX* (portion of registration number is excluded for personal data protection reasons) and Euro 5 standards which was measured at 42 kilometres in D1 highway in the direction towards Prague. This truck was chased by our vehicle for a short time period from 13:11:20 to 13:12:15 on 3rd of June. The overall concentration measured for this truck were divided in to five intervals which are represented in 5 red circles in the *figure5.3 (left)*. The *figure 5.3 (right)* shows the linear regression curve of the left graph which gives overall emission ratio of NO_x with respect to CO_2.

The *Figure 5.4* shows the individual separate events from *figure 5.3* which were represented in red circles in order to show the perfect area of peak which corresponds exactly to the high concentration.

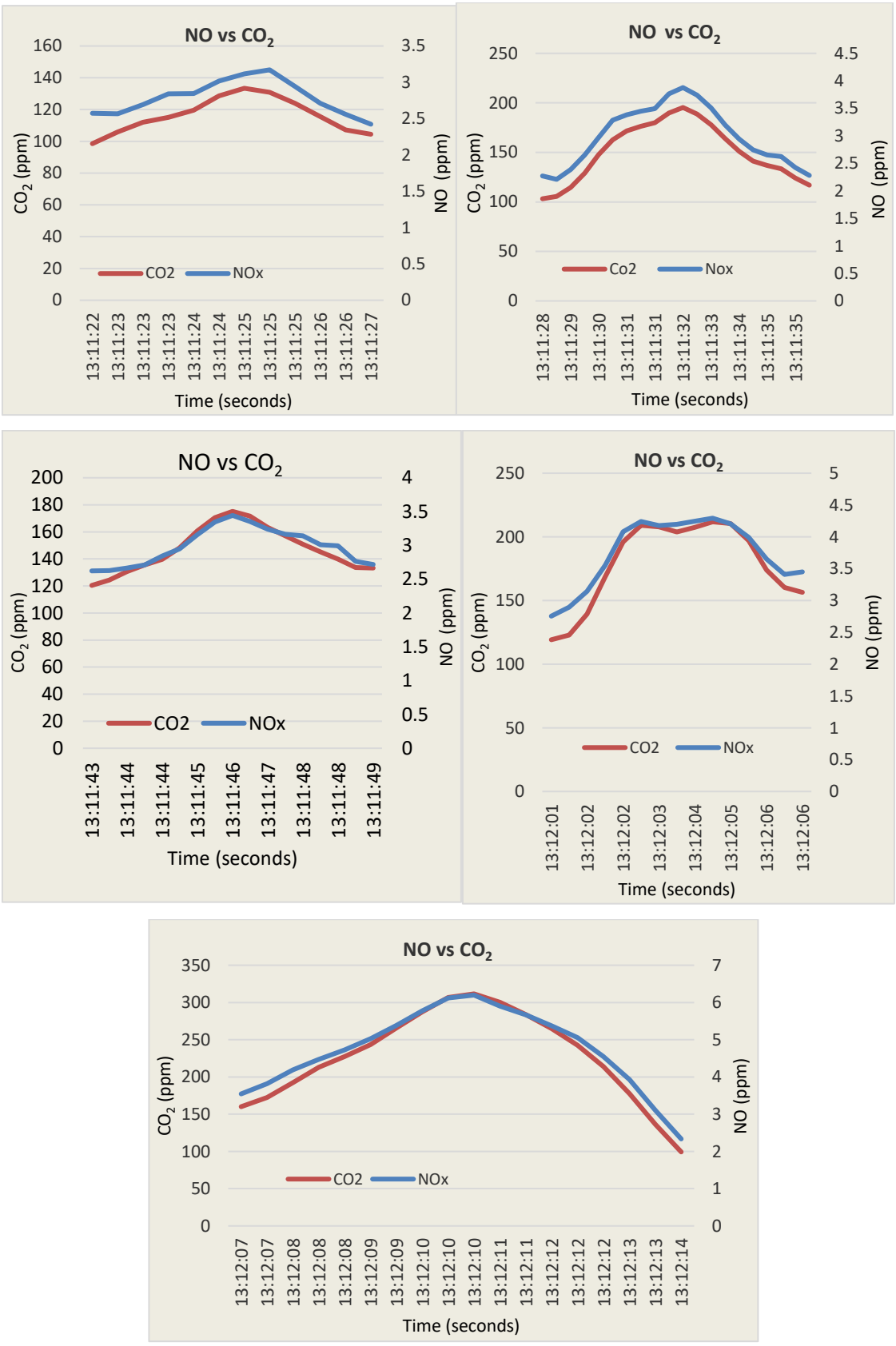

Fig 5. 4 Peak areas of figure 5.3 divided in to five intervals

5.3 Maximum NO to Maximum CO_2 approach

This approach is used to get the useful maximum value or the peak concentration of NO from the selected regime above the detection limit. In this approach, maximum value of NO and CO_2 are selected and then the ratio of NO and CO_2 is calculated. This approach seems to be reasonable to get the maximum concentration of NO and CO_2 which can give the highest concentration of NO emitted by the vehicle. The Table 1.1 shows the peak or maximum concentration of NO and CO_2 from *Figure 5.4.*

Max NO (ppm)	Max CO_2 (ppm)	Max NO/CO_2
3.1	133	0.023
3.9	195	0.019
3.4	175	0.019
4.3	212	0.020
6.2	312	0.019

Table 5. 1Maximum NO to CO_2 from figure 5.4

5.4 Linear Regression approach

Regression approach is one of the other approaches which is used to find the emission factor or NO/CO_2 ratio with a better correlation by plotting the dependent variable of Oxides of Nitrogen (NO_x) with respect to independent variable of carbon dioxide (CO_2). The slope of this correlation gives the NO/CO_2 ratio which was almost similar when compared with the peak area approach.

Though the correlation from the *Figure 5.3 (right)* looks good, but still there are two events visible in this correlation graph which are differentiated by two different colored rectangles. This creates a question whether the same truck behaved in different manner or is it some manipulation device was switched for the performance of after treatment devices. It was more uncertain to predict the real root cause of the measured concentration. For the better visualization and analysis, these areas were divided separately as discussed before and that resulted in a better visibility. The below *figure 5.5* clearly gives a very good correlation between NO and CO_2. This truck measured during this period was one of the high emitters and their Emission ratio was compared with different approach to show consistency and better correlation.

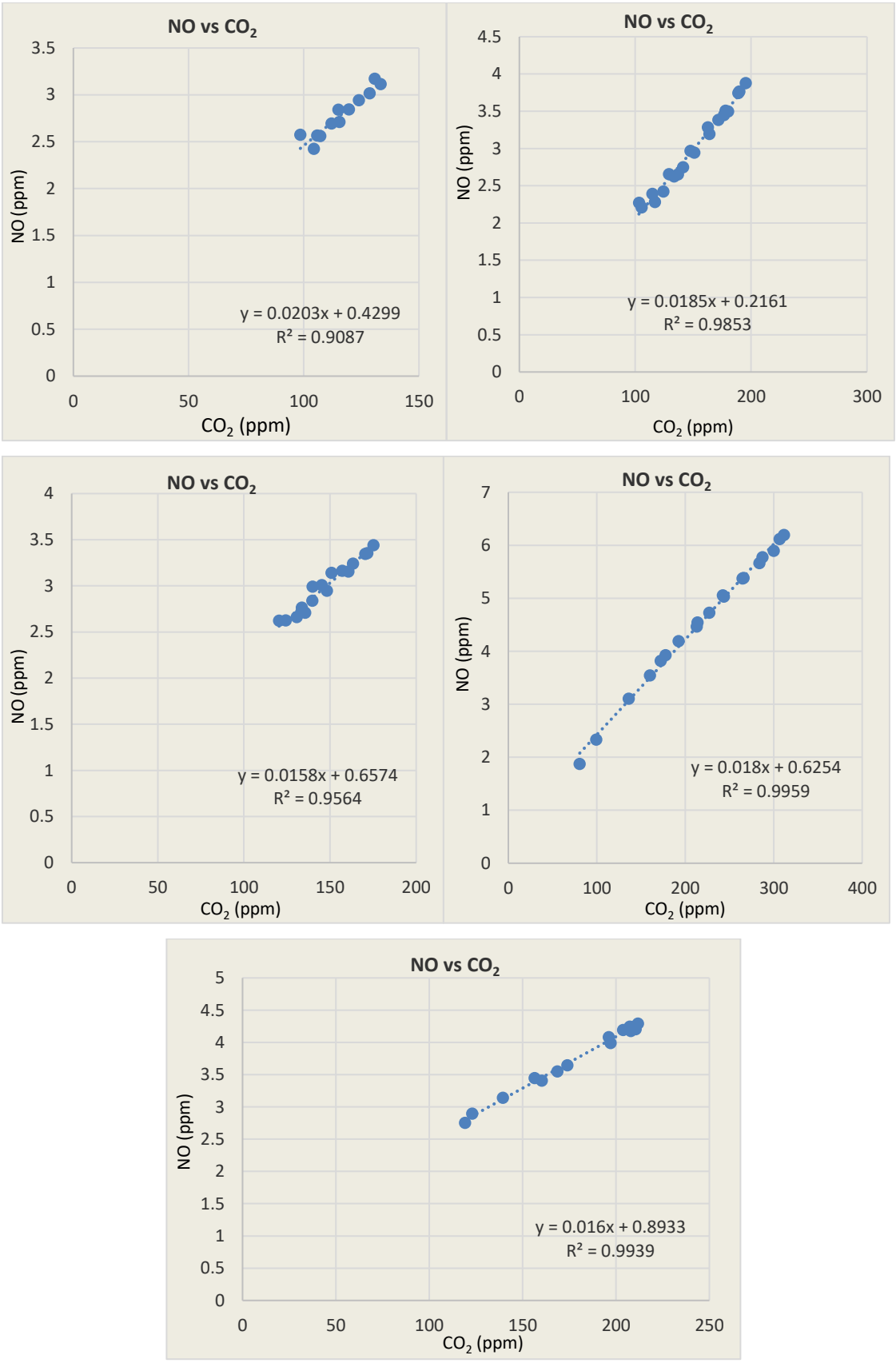

Fig 5. 5 Correlation of figure 5.6 divided in to five intervals for better Emission ratio

5.5 Comparison between these approaches

The considered areas for analysis were approached through two techniques as discussed before and they are compared with each other in order to check the consistency.

The peak areas of NO and CO_2 were analysed separately, and their ratio was calculated and were compared with the regression line approach in which the NO/CO_2 ratio is obtained from the slope. This emission ratio was found to be very similar between these approaches.

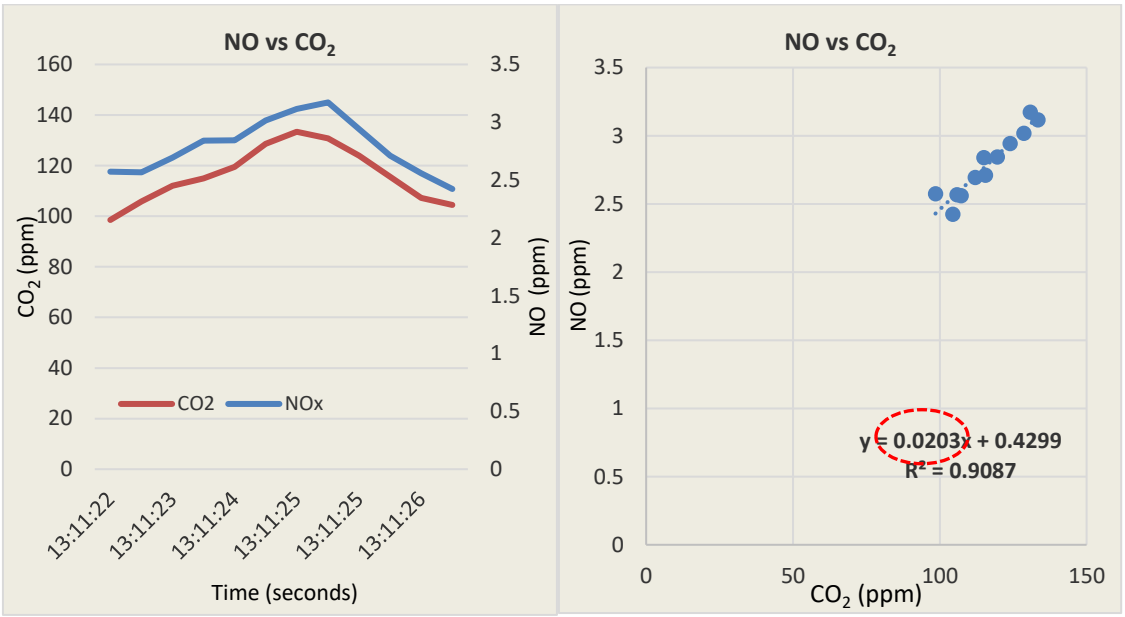

Fig 5. 6 Comparison of first peak of the above measurement with a good correlation

The above *Figure 5.6* gives the comparison between two approaches which was the measurement taken on 3rd of June from the vehicle number BH3XXXX with Euro 5 Standard. From *figure 5.6 (left)*, both the area of concentrations was calculated separately by integrating over the surface and the emission ratio were found to be as follows:

Area of NO from the curve = 33.4

Area of CO_2 from the curve = 1394

NO/CO_2 ratio = Area of NO / Area of CO_2

= 33.4/1394

= 0.0239

Max NO (ppm)	Max CO_2 (ppm)	Max NO/CO_2
3.1	133	0.0234

The red dotted circles mentioned above clearly indicates that the emission ratio evaluated from these approaches were found to be consistent. Similarly, other vehicles measurements were also compared. This NO/CO_2 ratio calculated for the *figure 5.6* from peak area approach was found to be 0.023, from regression line approach was found to be 0.020 and from maximum point of concentration was found to be 0.023 which shows a good consistency between these approaches.

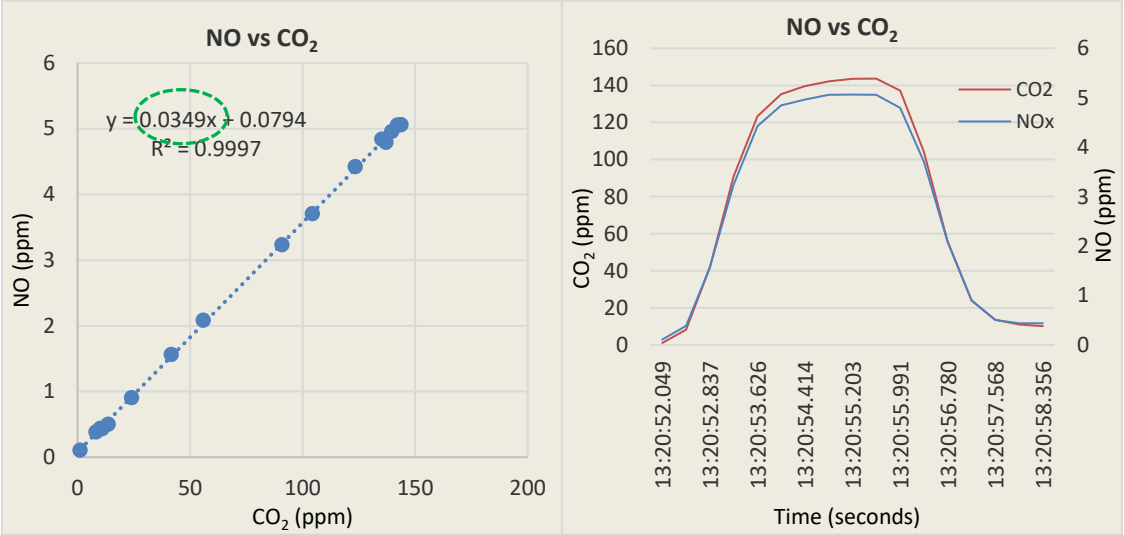

Fig 5. 7 Measurement from Euro 4 standard truck with vehicle number 3Z1XXXX measured on 3rd of June with a good correlation.

Area of NO from the right curve = 47.5

Area of CO_2 from the right curve = 1325

NO/CO_2 ratio = 0.0359

Max NO (ppm)	Max CO2 (ppm)	Max NO/CO2
5.06	143	0.0352

From the green circles shown in the above *figure 5.7*, in the equation and in the table, it's very clear that the better correlation gives a very good comparison and resembles almost the consistent NO/CO_2 ratio.

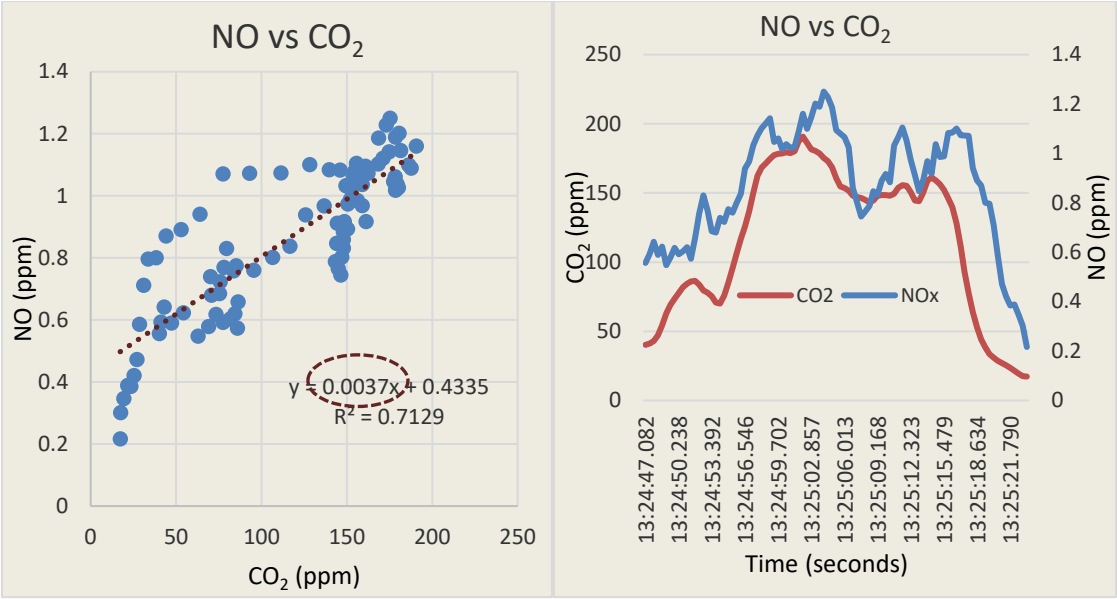

Fig 5. 8 Measurement from Euro 6 standard truck vehicle number 4ALXXXX.

The above *figure 5.8* shows the concentration of NO and CO_2 measured from a Euro 6 standard trucks on 3rd of June at 13:24:47 with a poor correlation. Comparison of NO/CO_2 from these approaches were found to have a higher difference when compared to the truck number 3Z1XXXX. This is clearly shown with the help of brown circles in the regression curve above, in the table and in the formulation below.

Area of NO from the right curve = 80.2

Area of CO_2 from the right curve = 10789

NO/CO_2 ratio = 0.0074

Max NO (ppm)	Max CO2 (ppm)	Max NO/CO2
1.25	190	0.00655

This NO/CO_2 ratio calculated for the *figure 5.8* by peak Area approach was found to be 0.0074, Regression line approach was found to be 0.0037. and Maximum peak concentration approach was found to be 0.0065 which shows poor consistency between these approaches.

5.6 Comparison of High, Low and Inconsistent Emitters

5.6.1 High NO emitters

Though many trucks were measured and analyzed, an example was taken to show the better correlation in which the following data projected in the graph shows a higher value in the

concentration of NO. This was a EURO 5 truck and the following graph shows that NO is very well correlated to CO_2. In peak area approach, two methods were used to find NO/CO_2 ratio. The first method was to find the area of CO_2 and area of NO separately and they are numerically integrated over the whole peak regime and the ratio of NO/CO_2 is evaluated. The second method was to find the maximum point of CO_2 in the whole area of the selected regime and then the corresponding NO is divided with the CO_2 peak to get their ratio which is represented in *figure 5.7* with a black circle. In linear regression approach represented in *figure 5.8*, the concentration of NO and the concentration of CO_2 were plotted against each other and the correlation was found. With the help of regression line approach, the ratio of NO to CO_2 is obtained from the slope. The emission ratio was evaluated for the three different approaches and the value looked quite consistent to each other and the NO emission factor was calculated, and it seems like a high value when compared with European Emission Standards. This is one of the best examples to show excess NO emitters from the measurements.

NO average (ppm)	CO_2 average (ppm)	slope (NO/CO_2) linear regression	Correlation R^2	NO (g/kWh)	NO/CO2 peak area approach	NO/CO2 maximum point approach
2.3	114	0.016	0.95	8.28	0.020	0.019

Table 5. 2 NO/CO_2 ratio comparison through various approach from truck 8U4XXXX

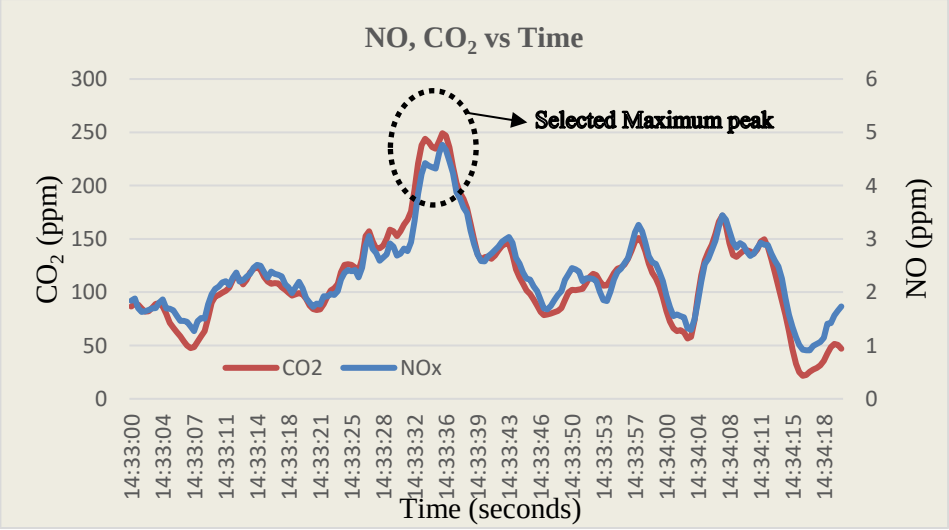

Fig 5. 9 NO and CO_2 measured over a period from truck 8U4XXXX

The black dotted circle from the above *Figure 5.9* shows the maximum concentration of both NO and CO_2 in which Emission ratio was calculated to check the consistency and are compared with other approaches.

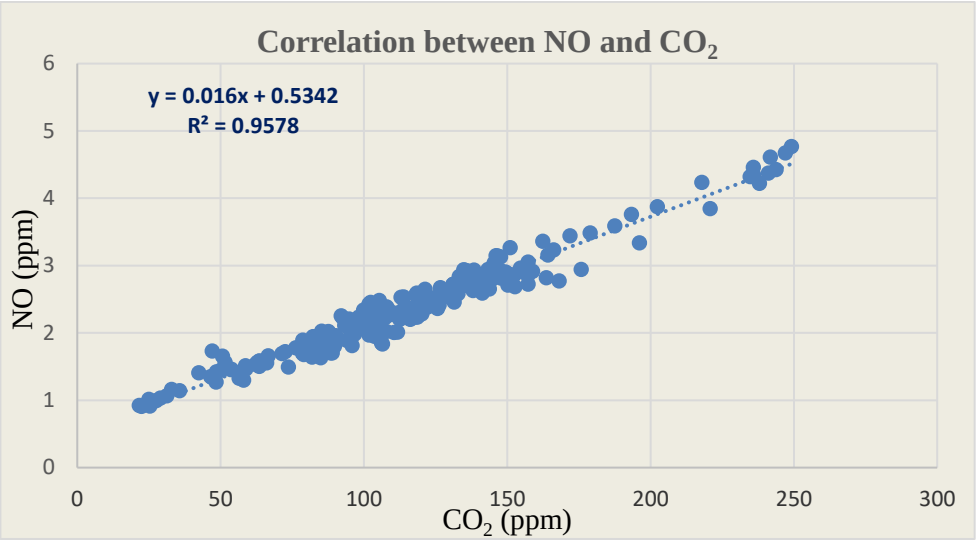

Fig 5. 10 Correlation between NO and CO_2 measured from truck 8U4XXXX

The above graphs in the *figure 5.9 and 5.10* shows the correlation between NO and CO_2 which was recorded on 3rd of June around 14:33:00 hours at 41 kilometres in the direction towards Prague on the D1 highway with the truck number 8U4XXXX. This had a very good correlation of 0.95 and NO to CO_2 ratio of 0.016. Higher correlation shows the closeness in the variation of both the concentration measured over a period.

5.6.2 Low NO emitters

Similarly, a low NO emitting truck shown in *figure 5.11 and 5.12* with vehicle number (AC6XXXX) CA0XXXX can be discussed through various approaches to calculate the NO to CO_2 ratio. This truck was EURO 6 standard European trucks and the corresponding correlation and Emission ratio was found to be very low when all these approaches were compared, still the NO concentration was found to be very low and this is the perfect example for low NO emitters measurement. This truck was found to have low NO concentration when compared to the vehicle with register number 8U4XXXX.

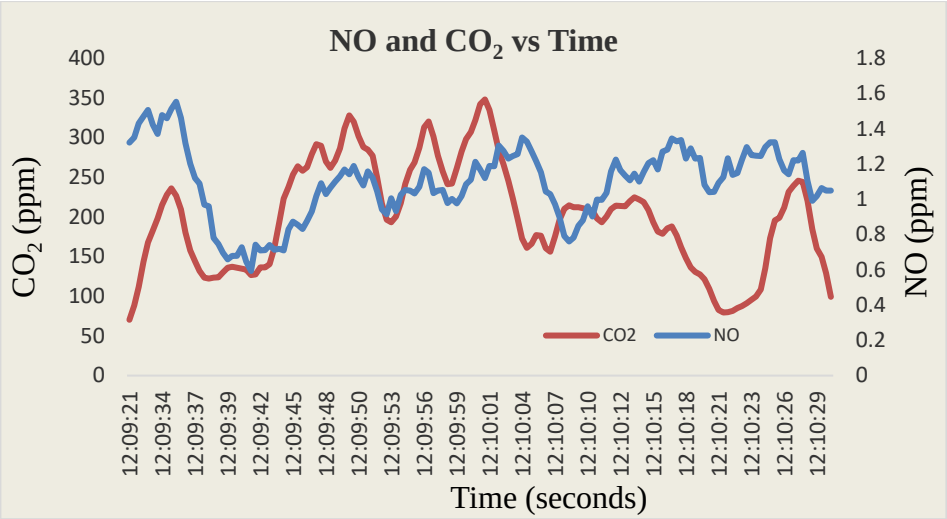

Fig 5. 11 NO and CO_2 measured over a period from truck CA0XXXX

NO average (ppm)	CO_2 average (ppm)	slope (NO/CO_2) linear regression	Correlation R^2	NO (g/kWh)	NO/CO2 peak area approach	NO/CO2 maximum point approach
1.09	199	0.00016	0.0030	0.102	0.0054	0.0044

Table 5. 3 NO/CO_2 ratio comparison through various approach from a truck AC6XXXX

From the above *Table 5.3*, it's very clear that the correlation was very poor, and it resulted in poor concentration of NO to CO_2 ratio. Though they are compared with three approaches, concentration of NO emission from this vehicle was found to be low.

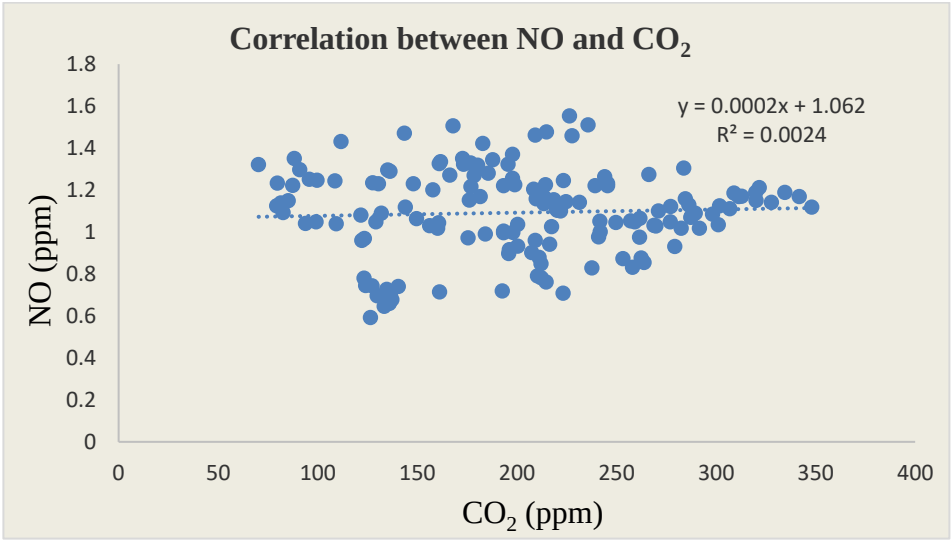

Fig 5. 12 Correlation between NO and CO_2 measured from a truck

5.6.3 Inconsistent NO emitters

From the measurements conducted, most of the measured data had a very good correlation which showed some vehicle with high NO, some with very low NO and some correlation were inconsistent. Inconsistency is due to many events happenings during the same period of measurement of a truck which creates uncertainty where three events are found which are plotted in *figure 5.14* with Red, Green and Blue dotted circles. These events are described in the following *figure 5.13 and 5.14*. Due to inconsistency, *table 5.4* also shows poor comparison of emission ratio of NO to CO_2 through different approach.

NO average (ppm)	CO_2 average (ppm)	slope (NO/CO_2) linear regression	Correlation R^2	NO (g/kWh)	NO/CO2 peak area approach	NO/CO2 maximum point approach
1.68	170	0.0024	0.17	1.265	0.0099	0.0072

Table 5. 4 NO/CO_2 ratio comparison through various approach from truck PA69XXXX

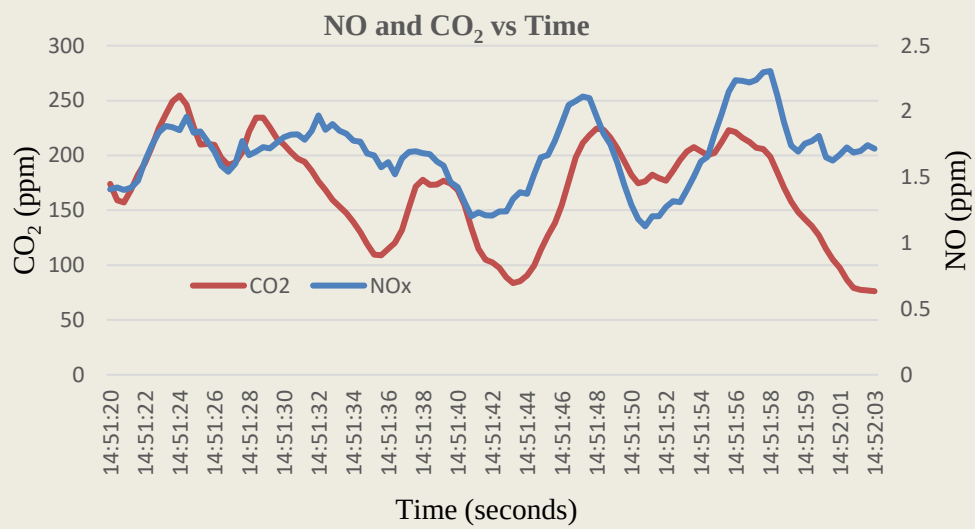

Fig 5. 13 NO and CO_2 measured over a period from truck PA69XXXX

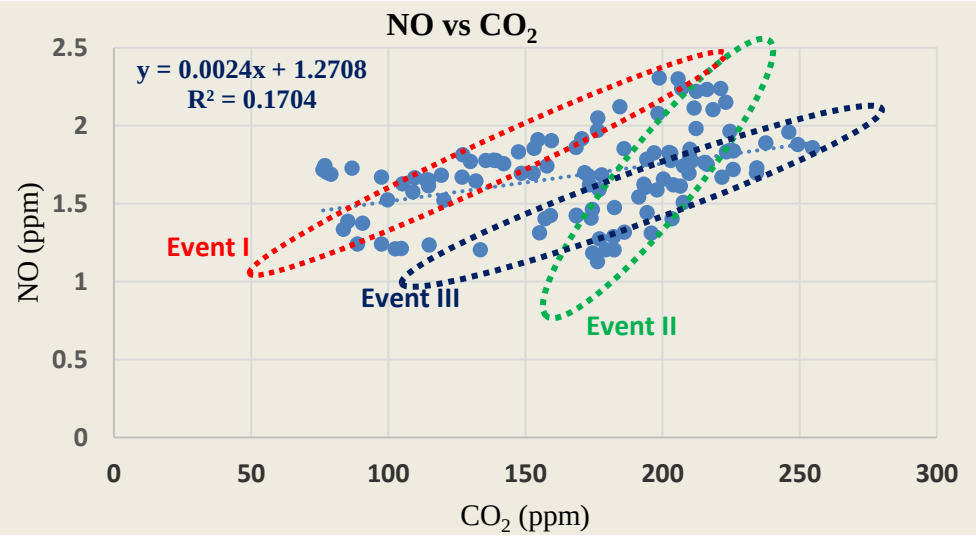

Fig 5. 14 Correlation between NO and CO_2 measured from truck PA69XXXX

The above graph in the *figure 5.14* clearly shows a poor correlation of 0.17 for all the three events measured from the truck PA69XXXX which was recorded on 4th of June around 14:51:00 hours at 19 kilometres in D1 motorway towards the direction of Prague. Due to the measurement uncertainty, two to three events with different NO/CO_2 ratio are seen. It can be due to the influence of different vehicles passed by the same side or in the opposite side or may be previous vehicles exhaust which was diluted and present in air or the same vehicle performed different way during the drive. This is more uncertain as it does not have a clarity what or where is the root cause from, as the driver's behaviour and any manipulation method inside the vehicle was not known, but only the European Standard of the vehicle was known from the toll transponder after giving the vehicle details which were noted while chasing the truck in our study.

5.7 Conversion of parts per million to grams per Kilowatt-hour

FT-IR spectroscopy used in our measurement were focused in measuring the concentration of NO and CO_2. Oxides of Nitrogen measured from the instruments used for measurements were in parts per million. In order to understand the emission produced per power produced by the engine, it is necessary to convert ppm to grams per kilowatt-hour (g/kWh) in which the current European legislation follows. This would give a clear understanding when compared with the current emission standards. The formula used for this conversion is as follows;

$$\text{Oxides of Nitrogen (g/kWh)} = \frac{[NO] * 46 * 698}{[CO2] * 44}$$

[NO] – Concentration of Oxides of Nitrogen (ppm)

[CO_2] – Concentration of Carbon dioxide (ppm)

Nitrogen dioxide (NO_2) has a molecular weight of 46 grams.

Carbon dioxide (CO_2) has a molecular weight of 44 grams

698 is the constant that represents grams of CO_2 per Kilo Watt hour power (g/kWh).

To get the absolute amount, concentration of gases is multiplied with their corresponding molecular weight. The main assumption considered for this constant conversion is Brake Specific Fuel consumption as 220g/kWh. This is a good assumption as the engine was running with load. Fuel has mass fraction of Carbon. 86% of the mass fraction of carbon in fuel is assumed to be oxidised which is equal to 698 g/kWh.

But later, based on the validation/empirical calibration done after the measurement, an additional correction factor of 0.843 was applied to calculate the NO concentration [41]. After applying correction factor, the above equation to calculate NO concentration is recalculated as,

$$\text{NO [g/kWh]} = \frac{[NO] * 46 * 588}{[CO2] * 44}$$

5.8 Comparison of various approaches

The ratio of NO to CO_2 is calculated through three different approaches like Peak area approach, Linear Regression approach and Maximum point of concentration in the peak area approach. An interesting thing noted from these comparisons was that the better the correlation of NO and CO_2 from the linear regression approach, closeness is the value of NO/CO_2 ratio through all the three approaches. If the correlation is very poor from the regression analysis, then the ratio of NO and CO_2 through the three different analysis had a major difference among each other. The summary of comparison of Emission ratio of a few trucks is mentioned in the *Table 5.4* as follows:

NO average (ppm)	CO_2 average (ppm)	Emission ratio (NO/CO_2) linear regression	Correlation R^2	NO (g/kWh)	NO/CO2 peak area approach	NO/CO2 maximum point approach	NO average g/kWh	NO peak g/kWh
0.55	70.2	0.0016	0.31	0.97	0.0078	0.0019	4.84	1.20
0.78	72.1	-0.0045	0.35	-2.76	0.0107	0.0044	6.62	2.72
0.55	154.2	-0.0001	0.00	-0.08	0.0035	0.0034	2.19	2.10
2.76	127.8	0.0137	0.87	8.43	0.0216	0.0198	13.29	12.21
3.73	175.6	0.0184	1.00	11.30	0.0212	0.0198	13.29	12.21
2.98	82.9	0.0348	1.00	21.39	0.0359	0.0352	22.08	21.67
0.86	116.6	0.0038	0.71	2.32	0.0074	0.0065	4.57	4.03
1.32	105.0	0.0067	0.97	4.13	0.0126	0.0106	7.77	6.54
1.43	135.6	0.0069	0.95	4.25	0.0105	0.0091	6.50	5.64
0.40	222.8	0.0113	0.79	6.96	0.0017	0.0021	1.07	1.31
1.35	129.4	0.0039	0.87	2.40	0.0104	0.0074	6.45	4.61
0.99	268.6	0.0038	0.96	2.37	0.0036	0.0037	2.27	2.31
0.70	302.0	0.0028	0.82	1.74	0.0023	0.0022	1.43	1.39
1.52	162.4	0.0074	0.87	4.57	0.0093	0.0084	5.75	5.19
2.36	114.2	0.0160	0.96	9.81	0.0206	0.0191	12.69	11.76
2.12	140.8	0.0095	0.93	5.83	0.0192	0.0191	11.84	11.76
1.69	218.2	0.0103	0.93	6.31	0.0077	0.0098	5.75	6.04
2.12	126.1	0.0095	0.96	5.86	0.0170	0.0136	10.46	8.41
3.40	208.9	0.0128	0.92	7.86	0.0162	0.0140	5.75	8.63
2.29	142.9	0.0121	0.93	7.43	0.0160	0.0145	9.90	5.19
1.00	155.6	0.0033	0.38	2.06	0.0064	0.0049	3.94	3.07
2.36	220.0	0.0084	0.90	5.19	0.0107	0.0103	6.60	6.37
2.08	196.4	0.0067	0.87	4.11	0.0106	0.0091	6.53	5.64
1.03	187.9	0.0032	0.96	1.95	0.0054	0.0038	3.36	5.19
3.87	178.1	0.0176	0.98	10.82	0.0217	0.0194	13.45	11.93
0.53	267.4	-0.0004	0.07	-0.26	0.0019	0.0021	1.20	1.32
2.02	122.2	0.0091	0.86	5.59	0.0167	0.0134	10.32	8.25
4.56	175.0	0.0233	0.99	14.34	0.0260	0.0245	16.02	15.10
1.87	326.6	0.0041	0.87	2.53	0.0057	0.0046	3.52	2.83
3.81	107.3	0.0299	0.96	18.37	0.0354	0.0329	21.80	20.23
1.93	315.0	0.0080	0.94	4.90	0.0061	0.0068	3.78	4.18
1.50	209.4	0.0071	0.86	4.38	0.0071	0.0080	4.42	4.98
2.72	310.0	0.0061	0.92	3.76	0.0087	0.0074	5.38	4.61
2.34	203.7	0.0110	0.88	6.75	0.0114	0.0116	7.04	7.19
1.50	177.2	0.0056	0.96	3.43	0.0084	0.0067	5.18	4.14
1.60	215.0	0.0075	0.86	4.62	0.0074	0.0075	4.59	4.63
0.83	190.8	0.0000	0.32	0.00	0.0043	0.0034	2.65	2.10
0.98	161.5	0.0000	0.01	-0.02	0.0060	0.0061	3.74	3.80
3.95	293.0	0.0096	0.80	5.91	0.0135	0.0125	8.31	7.71
2.28	186.6	0.0079	0.91	4.88	0.0123	0.0104	7.56	6.44
0.76	172.9	-0.0012	0.05	-0.72	0.0043	0.0053	2.68	3.32
2.57	194.7	0.0098	0.92	6.04	0.0132	0.0112	8.12	6.89
2.66	262.6	0.0081	0.92	5.00	0.0101	0.0106	6.22	6.57

5.37	236.3	0.0178	0.96	10.93	0.0227	0.0203	13.96	12.52
0.59	252.8	-0.0009	0.10	-0.57	0.0023	0.0026	1.44	1.61
0.33	246.4	-0.0004	0.02	-0.25	0.0013	0.0018	0.82	1.12
1.47	435.8	0.0023	0.88	1.41	0.0033	0.0022	2.07	1.41
5.11	220.5	0.0219	0.91	13.46	0.0231	0.0229	14.24	14.10
3.92	366.1	0.0111	0.94	6.84	0.0107	0.0101	6.59	6.26
2.07	321.2	0.0049	0.99	3.04	0.0064	0.0056	3.96	3.45
1.25	127.5	0.0098	0.84	6.04	0.0097	0.0100	6.00	6.19
1.75	308.1	0.0038	0.93	2.37	0.0056	0.0051	3.49	3.14
2.67	443.3	0.0055	0.87	3.41	0.0060	0.0058	3.71	3.61
1.96	272.8	0.0049	0.88	3.01	0.0071	0.0063	4.42	3.88
0.69	227.9	-0.0002	0.00	-0.13	0.0030	0.0021	1.86	1.35
1.75	192.6	-0.0029	0.07	-1.78	0.0090	0.0037	5.58	2.32
3.01	149.6	0.0178	0.92	10.95	0.0201	0.0194	12.39	11.93
2.44	155.9	0.0127	0.90	7.78	0.0156	0.0145	9.61	8.93
4.34	225.5	0.0191	0.98	11.74	0.0192	0.0185	11.83	11.43
4.03	177.3	0.0175	0.88	10.77	0.0226	0.0224	13.96	13.82
2.12	114.0	0.0155	0.88	9.55	0.0185	0.0138	11.41	8.50
1.83	245.9	0.0074	0.82	4.52	0.0074	0.0067	4.59	4.12
3.43	151.3	0.0199	0.94	12.26	0.0226	0.0218	13.91	13.44
3.79	186.0	0.0169	0.90	10.40	0.0203	0.0196	12.51	12.07
0.81	215.8	-0.0008	0.02	-0.51	0.0037	0.0023	2.31	1.47
2.45	271.6	0.0083	0.91	5.12	0.0090	0.0085	5.55	5.27

Table 5. 5 Comparison of NO to CO2 ratio with different approaches for a few trucks

From the above summary in *table 5.5*, First and the second column corresponds to the measured data and the third column is the ratio of NO to CO_2 obtained by the analysis through linear regression approach, fourth column corresponds to the correlation obtained through linear regression line when plotted NO against CO_2, fifth column corresponds to the NO_x concentration calculated from the Emission ratio through linear regression method sixth and seventh column corresponds to the ratio of NO/CO_2 obtained from peak area approach and maximum concentration point in the selected regime and the last two columns corresponds to the NO_x concentrations calculated from these two approaches. Blue colour highlighted data are the ratio of NO to CO_2 comparison of some truck data through different approaches. As these had a higher correlation, NO/CO_2 ratio was found to be consistent when compared with all the three different approaches. This also shows that most of the higher correlation correspond to higher concentration of NO with few exceptions.

In addition to this, some of the values of NO was found to be negative which is highlighted in red in the *Table 5.5*. These negative values are due to very poor correlation which lead to

obtain a negative slope value in calculation of ratio of NO to CO_2 by the linear regression approach. This negative slope value gave a negative concentration of NO. So, the peak area approach was selected to get the positive value of Emission ratio which is a reasonable measure for the concentration of NO.

5.9 Summary of High Emitters

High emitters can be described in many perspectives, all concentrations of harmful emissions above certain limit are going to destroy human health and the environment irrespective of the vehicles measured and the corresponding Euro standards which are implemented in the concerned vehicle. When considering emissions from individual Euro standards of the vehicle, the allowable Emission limit varies for different standard trucks. The latest followed limit is Euro 6. From these, the emission of NO_x above the Euro 6 limit is acceptable by Euro 5 vehicle and other vehicle with lower Standards. But still they are harmful to human health and environment as discussed before.

There were about 235 vehicles measured during this measurement campaign and of these 31 vehicles were found to have concentration of NO which are mentioned in the below table 5.6 and in the figure 5.15. This clearly shows that high concentration of NO is found in all standards of European trucks, so one of the possibilities is some manipulation techniques is functioning or there are some tampering methods performed in this vehicle. Almost all these high emitters had a very good correlation which leads to high NO to CO_2 ratio that corresponds to high emissions of NO_x.

Euro	Vehicle number	D1 km	Time	NO (ppm) average	CO_2 (ppm) average	NO/CO_2	R^2	NO g/kWh
E6	ZA7XXXX	54	10:30:45	3.49	206	0.016	0.68	9.92
E6	WZ4XXXX	54	12:53:40	3.81	107	0.030	0.96	18.37
E6	(5Z60XXX) 5Z6XXX	34	14:03:06	2.34	204	0.011	0.88	6.75
E6	7C7XXXX (7C2XXXX)	48	14:34:30	1.74	379	0.013	0.43	8.12
E6	3SPXXXX (3SMXXXX)	50.5	09:40:19	4.44	149	0.023	0.80	14.37
E6	BH6XXXX (BH4XXXX)	53.2	12:27:22	3.64	166	0.019	0.61	11.82
E6	NPOXXXX	48	10:23:45	3.01	150	0.018	0.92	10.95
E5	BH 3XXXX	42	13:11:56	2.76	128	0.014	0.87	8.43
E5	BH 30XXX	42	13:12:15	3.73	176	0.018	1.00	11.30
E5	8U4XXXX	41	14:34:20	2.36	114	0.016	0.96	9.81
E5	AT31XXXX	26.5	14:45:22	3.40	209	0.013	0.92	7.86
E5	BR76XXXX	44	09:58:10	3.87	178	0.018	0.98	10.82

E5	(AC3XXXX) CA0XXXX	46	14:33:28	4.29	218	0.018	0.78	11.12
E5	DS00XXX (DS4XXXX)	51	14:38:55	5.37	236	0.018	0.96	10.93
E5	BH61XXX(BH59XXX)	43.5	10:58:21	5.11	221	0.022	0.91	13.46
E5	B610XXXX	43	09:16:05	4.76	166	0.020	0.72	12.21
E5	VL1XXXX	31	10:58:38	4.34	226	0.019	0.98	11.74
E5	E7XXXX	46	11:09:57	4.03	177	0.018	0.88	10.77
E5	BG6XXXX	33	12:49:21	1.14	57	0.019	0.64	11.41
E4	3Z1XXXX	35	13:20:58	2.98	83	0.035	1.00	21.39
E4	B14XXXX	46	11:07:40	4.56	175	0.023	0.99	14.34
E4	8A9XXXX	45	13:30:29	3.26	194	0.015	0.76	9.00
E4	2ABXXXX (3S9XXXX)	18	12:30:11	3.91	197	0.013	0.71	8.04
E4	4J2XXXX	37	10:48:29	2.44	156	0.013	0.90	7.78
E3	7POXXXX	41	10:44:30	7.03	418	0.016	0.18	9.66
E3	TO9XXXX (TO1XXX)	40	13:05:45	1.68	117	0.015	0.61	9.18
E3	5A9XXXX	35	09:20:04	1.84	66	0.025	0.57	15.08
E3	BB4XXXX	36	10:04:59	1.23	97	0.016	0.76	9.93
E3	TPBXXXX	38	12:39:29	2.12	114	0.016	0.88	9.54
E..	6ALXXXX	52	13:08:36	3.43	151	0.020	0.94	12.26
E2	8S2XXXX	38	13:17:33	3.79	186	0.017	0.90	10.40

Table 5. 6 Summary of high emitters

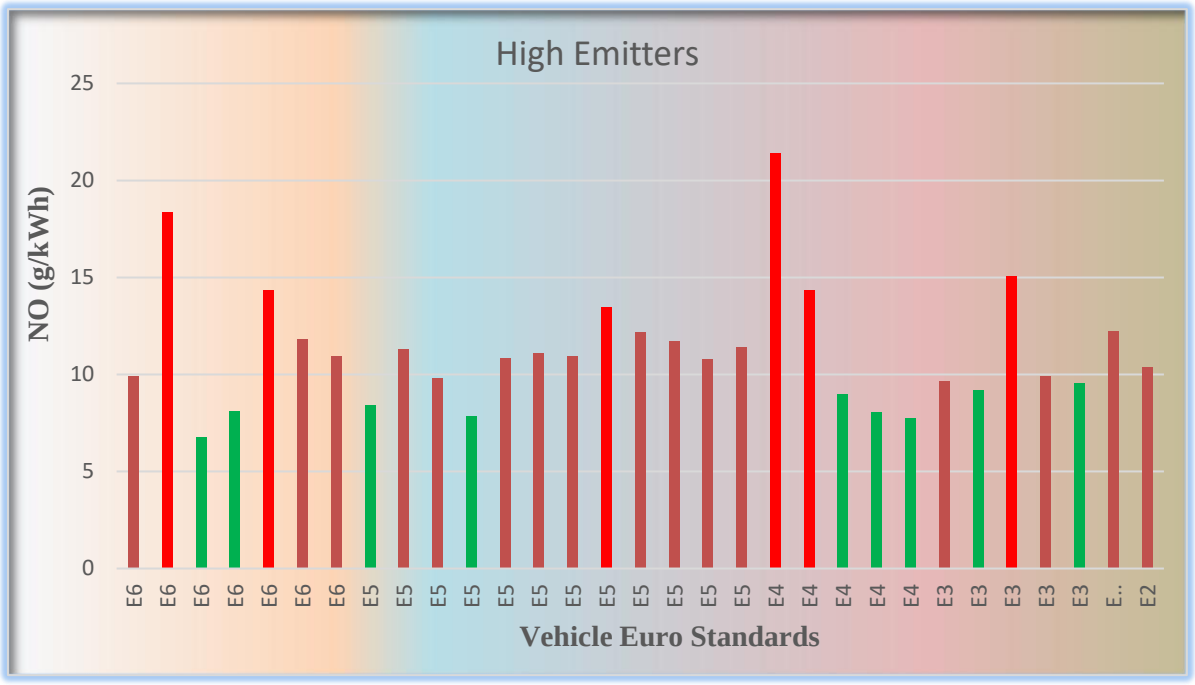

Fig 5.15 Range of Excess concentration of NO from higher correlation from Tab 5.6

From the above *Figure 5.15*, all European Standard trucks from Euro 2 to Euro 6 were falling in the category of high emitters. The red line from the above figure indicates the highest emitters when compared with other high emitting vehicles which are from the vehicle with

their details WZ4XXXX (Euro 6), 3SPXXXX (3SMXXXX (Euro 6)), BH6XXXX (BH5XXXX (Euro 5)), 3Z1XXXX (Euro 4), B14XXXX (Euro 4) and 5A9XXXX (Euro 3). Though other vehicles were also emitting high, but they were quiet less compared to the above mentioned vehicle details.

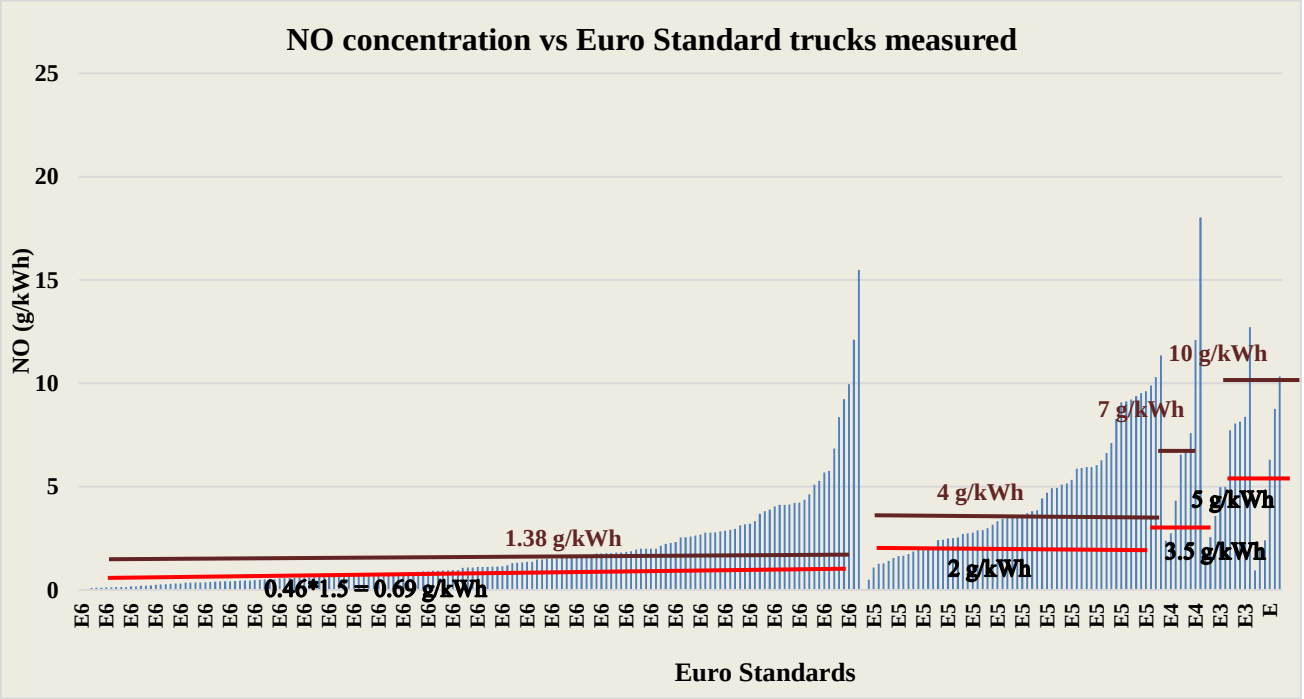

Fig 5.16 Measured vehicles and their Emission limit of NO to Euro Categories

The above *figure 5.16* shows the overall measured trucks during the experimental campaign and their corresponding Euro categories with NO_x concentration. They are represented in the sequence of Euro 6, Euro 5 and so on. The red line indicates the European Emission limit which are in current legislation. But they are multiplied with conformity factor of 1.5 in which the real drive emission is different from the measurements in the laboratory. But quite a higher concentration of NO_x is found to be there from the measurement data. So, around twice above the European legislation are assumed as excess emitters in which still some of the measured vehicles from all the Euro Standards fall in to this category. These are represented in horizontal brown line in the above *figure 5.16.* The summary of entire measurements is discussed in chapter 6.1. Most of the measured vehicle were Euro 6 and of these, majority of the vehicles were within the NO_x emission limit. So possibly, the SCR installed in these new trucks were functioning effectively. And the other measured trucks were having higher concentration of NO above the NO_x emission limit.

6 Measurement description

The measurement was conducted for a week from 3rd of June to 7th of June 2019 in D1 highway on both the direction of Prague and Brno in which Heavy Duty Trucks were chased by Vehicle chase method in order to find the real drive emission in concern with Environmental pollution and human health. Almost 235 trucks were measured during this campaign in which the vehicle details were noted when they were being chased and the corresponding European Emission Standards of the vehicle were obtained from the toll centers after giving the noted vehicle details.

6.1 Summary of Measurement

The below *Table 6.1* clearly summarizes the vehicle details noted during the measurement campaign with the corresponding Euro Standard of the vehicle along with the kilometer mentioned in D1 highway for better comparison with road profile, with the time measured for better comparison with the recorded measurement, direction of travel and concentration of undesired emission of Oxides of Nitrogen (NO_x) with respect to desired product of combustion of fuel in an Internal Combustion Engine which is Carbon dioxide (CO_2). Of these, some of the vehicle number and details were repeated in the table mentioned. This is shown in such a way as each of the data gave a very good specific correlation in showing the emission ratio. Also, some of the data are highlighted in red which clearly indicates that the truck details like vehicle number or Euro standards missed during the measurement. To avoid providing the wrong information, the illegible or missed data are highlighted in red color and are not mentioned. Also, some of the vehicle details are not known as they were not legible and so they were not written.

Further, in the *Table 6.1* which is mentioned below has a few NO concentrations in negative or negligible amount. This is mostly exhibited by very rare Euro 6 trucks which gives a negative Emission ratio or slope in the regression curve. This negative slope or negligible fraction possibly indicates that these vehicles are well within the limit which emits very less amount of NO_x and so these trucks mostly are following the legislations which is concerned mostly on human health and environment.

DATE	EURO STD	VEHICLE DETAILS	D1 (KM) HIGHWAY	TIME	NO avg (ppm)	CO_2 avg (ppm)	NO/CO_2 (linear regression)	R^2	NO g/kWh
JUNE 3 PM	E6	9B7XXXX	24-29	12:51:14	0.55	70	0.0016	0.31	0.97
	E6	A09XXXX	33	12:53:00	0.78	72	-0.0045	0.35	2.76
	E5	3J7XXXX	40	12:59:12	0.76	24	0.0115	0.22	7.06
	E6	1BRXXXX	47	13:05:06	0.55	154	-0.0001	0.00	2.10
	E5	BH3XXXX	42	13:11:56	2.76	128	0.0137	0.87	8.43
	E5	BH3XXXX	42	13:12:15	3.73	176	0.0184	1.00	11.30
	E4	3Z1XXXX	35	13:20:58	2.98	83	0.0348	1.00	21.39
	E6	4ALXXXX	30	13:25:23	0.86	117	0.0038	0.71	2.32
	E5	NP0XXXX	33	13:26:44	1.32	105	0.0067	0.97	4.13
	E5	NP0XXXX	33	13:27:16	1.43	136	0.0069	0.95	4.25
	E5	F7XXXX	30	13:37:14	0.4	223	0.0113	0.79	6.96
	E6	4ATXXXX	39	13:44:00	0.51	35	0.0017	0.01	1.03
	E5	MUXXXX	47	13:47:46	1.35	129	0.0039	0.87	2.40
	E5	MVXXXX	43	13:55:19	0.88	312	0.0001	0.00	0.06
	E6	ME5XXXX	37	13:58:57	0.63	147	0.0018	0.11	1.12
	E6	PAXXXX	31	14:07:46	0.99	269	0.0039	0.96	2.37
	E6	PAXXXX	31	14:07:59	1.04	399	0.0017	0.67	1.04
	E6	PAXXXX	31	14:09:38	0.7	302	0.0028	0.82	1.74
	E5	4J2XXXX	40	14:16:47	1.5	190	0.0047	0.68	2.87
	E5	4J2XXXX	40	14:17:31	1.52	162	0.0074	0.87	4.57
	E6	19JXXXX	45	14:21:59	0.77	73	0.0034	0.18	2.10
	E6	PAXXXX	48	14:23:12	0.74	262	0.0013	0.53	0.78
	E6	7C6XXXX	51	14:26:16	1	314	0.0032	0.69	1.94
	E6	1BNXXXX	49	14:29:00	0.89	144	0.0034	0.63	2.12
	E5	8U4XXXX	41	14:34:20	2.36	114	0.0160	0.96	9.81
	E5	8U4XXXX	41	14:31:53	2.12	141	0.0095	0.93	5.83
	E5	3SYXXXX	19	14:36:24	1.69	218	0.0103	0.93	6.31
	E5	ATXXXX	26.5	14:44:17	2.12	126	0.0095	0.96	5.86
	E5	ATXXXX	26.5	14:45:22	3.4	209	0.0128	0.92	7.86
	E5	ATXXXX	26.5	14:46:07	2.29	143	0.0121	0.93	7.43
	E5	3S4XXXX	19	14:51:58	1	156	0.0033	0.38	2.06
JUNE 4 AM	E6	…..	29	09:28:00	0.48	178	0.0039	0.68	2.38
	E5	…..	34	09:35:10	1.77	128	0.0072	0.51	4.40
	E6	P05XXXX	44	09:39:00	2.36	220	0.0084	0.90	5.19
	E5	FSUXXXX	47	09:40:35	2.08	196	0.0067	0.87	4.11
	E6	PN8XXXX	55	09:44:10	0.81	151	0.0008	0.05	0.50
	E6	XZXXXX	52	09:51:23	1.13	274	0.0002	0.01	0.13
	E5	WBXXXX	50	09:52:56	1.03	188	0.0032	0.96	1.95
	E5	BRXXXX	44	09:58:10	3.87	178	0.0176	0.98	10.82
	E6	6CZXXXX	41	09:59:43	0.8	294	0.0010	0.50	0.61
	E5	WCXXXX	38	10:02:31	1.03	148	0.0010	0.03	0.58
	E6	5M6XXXX	29	10:14:27	0.83	190	0.0051	0.74	3.13
	E6	WAXXXX	33	10:15:07	0.53	267	-0.0004	0.07	1.32
	E6	XZXXXX	39	10:21:00	1.2	137	0.0061	0.59	3.77
	E5	ABXXXX	46	10:24:23	1.96	240	0.0027	0.38	1.68
	E6	ZA7XXXX	54	10:30:45	3.49	206	0.0161	0.68	9.92
	E6	B15XXXX	52	10:36:31	0.96	236	0.0004	0.03	0.23
	E6	1B1XXXX	50	10:38:20	0.84	99	0.0050	0.71	3.06

	E5	4SKXXXX	43	10:41:57	2.02	122	0.0091	0.86	5.59
	E6	SV3XXXX	41	10:44:30	0.82	170	0.0022	0.57	1.33
	E6	DZAXXXX	37	10:47:11	0.73	258	0.0001	0.00	0.04
	E6	5Z4XXXX	31	10:57:15	0.77	285	0.0013	0.39	0.78
	E6	3SKXXXX	33	10:58:35	0.75	134	0.0007	0.05	0.44
	E6	5AJXXXX	39	11:04:10	0.85	110	0.0012	0.08	0.73
	E4	B14XXXX	46	11:07:40	4.56	175	0.0233	0.99	14.34
	E6	B7XXXX	54	11:11:55	0.97	166	0.0032	0.50	1.98
	E6	LEXXXX	52	11:18:29	1.87	327	0.0041	0.87	2.53
	E6	CEXXXX	50	11:19:53	0.88	186	0.0008	0.24	0.50
JUNE 4 PM	E6	C2XXXX	44	12:26:48	0.77	153	0.0018	0.11	1.10
	E6	5Z1XXXX	29.5	12:37:33	1.4	225	0.0027	0.27	1.63
	E6	BL6XXXX	33	12:39:27	0.86	120	0.0006	0.02	0.38
	E6	RZ0XXXX	40	12:44:05	0.67	134	0.0035	0.12	2.15
	E6	JMXXXX	45	12:47:29	0.6	120	0.0005	0.02	0.32
	E6	VRXXXX	47	12:48:58	1.27	175	0.0061	0.64	3.72
	E6	JJXXXX	50	12:49:51	0.42	97	0.0016	0.08	0.98
	E6	WZ4XXXX	54	12:53:40	3.81	107	0.0299	0.96	18.37
	E6	……	53	12:58:05	1.46	175	0.0055	0.79	3.36
	E6	NXXXXX	43	13:05:14	1.57	182	0.0039	0.59	2.37
	E6	MSXXXX	42	13:06:37	1.86	184	0.0050	0.59	3.04
	E6	9B7XXXX	37	13:08:53	0.33	113	0.0002	0.00	0.14
	E6	9BXXXX	29	13:17:54	1.36	243	0.0013	0.10	0.77
	E6	3AXXXX	31	13:19:11	1.93	315	0.0080	0.94	4.90
	E6	HHXXXX	40	13:24:03	0.87	149	0.0003	0.00	0.17
	E4	8A9XXXX	45	13:30:29	3.26	194	0.0146	0.76	9.00
	E5	8T0XXXX	56	13:35:56	1.07	107	0.0100	0.71	6.13
	E6	NZXXXX	52	13:42:18	1.5	209	0.0071	0.86	4.38
	E5	PMXXXX	51	13:43:48	2.72	310	0.0061	0.92	3.76
	E6	WDXXXX	43	13:48:37	0.93	196	0.0012	0.02	0.72
	E5	ZV8XXXX	38	13:53:22	3.5	137	0.0115	0.47	7.05
	E5	4PXXXX	30	14:01:32	1.63	222	0.0064	0.74	3.95
	E6	5ZXXXX	34	14:03:06	2.34	204	0.0110	0.88	6.75
	E6	HCXXXX	40	14:07:54	0.74	147	0.0029	0.29	1.81
	E6	2CXXXX	45	14:11:40	2.46	283	0.0055	0.71	3.40
	E6	MAXXXX	47	14:13:32	1.72	286	0.0018	0.30	1.10
	E6	ADXXXX	49	14:14:16	1.36	238	0.0025	0.35	1.56
	E5	MT6XXXX	54	14:18:12	1.5	177	0.0056	0.96	3.43
	E6	WGXXXX	52	14:24:56	0.76	291	0.0012	0.43	0.72
	E6	RDXXXX	49	14:26:12	0.86	229	0.0003	0.03	0.20
	E6	1ZXXXX	43	14:31:07	0.81	128	0.0015	0.09	0.89
	E6	8BXXXX	37	14:34:51	0.86	239	0.0011	0.18	0.66
	E6	8B3XXXX	34	14:36:43	0.61	89	0.0013	0.04	0.81
	E6	3K4XXXX	21	14:49:49	1.6	215	0.0075	0.86	4.62
	E5	PAXXXX	19	14:52:03	1.69	170	0.0024	0.17	1.50
JUNE 5 AM	E6	BHXXXX	30	09:30:17	1.53	243	0.0034	0.11	2.09
	E6	B8XXXX	32	09:31:39	0.61	135	0.0003	0.06	0.16
	E6	PEXXXX	40	09:36:56	0.63	119	0.0026	0.10	1.57
	E6	1BXXXX	45	09:39:24	1.21	138	0.0052	0.48	3.18
	E5	2SXXXX	48	09:41:27	1.32	120	0.0070	0.68	4.32

	E6	1HXXXX	52	09:53:20	1.06	137	0.0035	0.00	2.16
	E5	5MXXXX	49	09:55:34	1.19	148	0.0048	0.05	2.96
	E6	SHXXXX	37	10:05:31	1.17	245	0.0022	0.00	1.36
	E6	POXXXX	30	10:13:59	2.55	291	0.0102	0.25	6.26
	E6	3SXXXX	33	10:15:15	0.47	139	0.0007	0.04	0.43
	E6	NZXXXX	40	10:20:57	1.08	243	0.0025	0.11	1.55
	E6	MMXXXX	46	10:24:40	1.85	151	0.0078	0.51	4.80
	E6	MMXXXX	48	10:24:59	3.07	331	0.0081	0.00	5.01
	E5	7SXXXX	55	10:31:36	2.49	149	0.0052	0.01	3.22
	E	EMXXXX	52	10:35:55	0.85	146	0.0018	0.63	1.12
	E5	ZBXXXX	51	10:37:43	1.78	181	0.0058	0.00	3.55
	E6	B4XXXX	43	10:43:10	0.83	191	0.0000	0.32	2.65
	E3	7PXXXX	41	10:44:30	7.03	418	0.0157	0.18	9.66
	E	AR1XXXX	30	10:55:18	1.17	141	0.0046	0.13	2.85
	E6	WDXXXX	31	10:56:23	0.95	136	0.0032	0.02	1.97
	E6	3SXXXX	39	11:02:06	0.98	162	0.0000	0.01	3.80
	E6	WCXXXX	44	11:05:49	2.69	241	0.0089	0.07	5.48
	E3	OPOXXXX	47	11:06:54	2.15	203	0.0069	0.05	4.26
	E6	WCXXXX	48	11:07:48	0.82	125	0.0017	0.19	1.07
	E6	ADXXXX	51	12:03:19	1.78	275	0.0056	0.55	3.45
	E6	4EXXXX	50	12:04:43	1.78	259	0.0049	0.74	3.02
	E3	3BXXXX	44	12:08:44	1.56	166	0.0034	0.42	2.10
	E6	ACXXXX	42	12:10:30	1.09	200	0.0002	0.00	0.10
	E3	13XXXX	37	12:14:20	3.95	293	0.0096	0.80	5.91
	E5	3ZXXXX	27	12:23:56	1.37	211	0.0053	0.71	3.25
	E6	WCXXXX	21	12:27:13	0.95	163	0.0011	0.02	0.67
	E4	2AXXXX	18	12:30:11	3.91	197	0.0131	0.71	8.04
	E6	KNXXXX	31	12:58:57	0.82	320	0.0009	0.34	0.54
	E6	ZHXXXX	32	12:59:54	1.09	193	0.0015	0.47	0.91
	E3	TOXXXX	40	13:05:45	1.68	117	0.0149	0.61	9.18
	E6	SEXXXX	46	13:09:07	1.81	293	0.0032	0.39	1.98
	E	PEXXXX	54	13:14:18	2.67	161	0.0122	0.72	7.48
	E6	9BXXXX	52	13:21:25	0.49	193	0.0007	0.02	0.43
JUNE 5 PM	E6	RBXXXX	50	13:22:56	0.8	219	0.0010	0.07	0.63
	E6	MAXXXX	43	13:27:00	1.34	138	0.0054	0.64	3.30
	E6	ECXXXX	41	13:28:12	1.37	221	0.0021	0.32	1.28
	E3	B3XXXX	38	13:31:26	3.16	193	0.0096	0.74	5.89
	E5	NSOXXXX	31	13:39:15	2.08	332	0.0054	0.77	3.29
	E5	MMXXXX	40	13:46:47	1.66	126	0.0114	0.58	7.00
	E6	CBXXXX	45	13:50:29	2.28	187	0.0079	0.92	4.88
	E6	POXXXX	54	13:56:26	0.76	173	-0.0012	0.05	3.32
	E6	ARXXXX	52	14:04:28	1.04	215	0.0015	0.05	0.92
	E6	WBXXXX	45	14:12:24	1.36	315	0.0016	0.28	0.96
	E5	BHXXXX	38	14:16:09	2.57	195	0.0098	0.92	6.04
	E6	CBXXXX	31	14:23:10	2.66	263	0.0081	0.92	5.00
	E6	TNXXXX	33	14:24:26	1.17	202	0.0014	0.19	0.84
	E5	ACXXXX	46	14:33:28	4.29	218	0.0181	0.78	11.13
	E6	7CXXXX	48	14:34:30	1.74	379	0.0132	0.43	8.12
	E5	DSXXXX	51	14:38:55	5.37	236	0.0178	0.96	10.93
	E6	BIXXXX	43	14:43:14	0.53	186	0.0008	0.17	0.51

	E6	BAXXXX	42	14:44:29	0.88	147	0.0018	0.20	1.08
	E6	TMXXXX	38	14:46:52	1.05	172	0.0028	0.20	1.75
	E6	LLXXXX	25	14:54:05	0.59	253	-0.0009	0.10	1.61
	E6	8CXXXX	21	14:57:32	0.33	246	-0.0004	0.02	1.12
	E6	WOXXXX	18	15:00:08	0.4	175	0.0008	0.15	0.48
JUNE 6 AM	E6	3SXXXX	50.5	09:40:19	4.44	149	0.0234	0.80	14.37
	E6	STXXXX	43	09:46:31	1.02	241	0.0012	0.04	0.71
	E6	XXXXXX	29	09:56:28	0.55	220	0.0005	0.18	0.32
	E6	PDXXXX	32.5	09:58:19	1.47	436	0.0023	0.88	1.41
	E6	LJXXXX	39	10:04:28	0.68	151	0.0016	0.14	0.97
	E5	LMXXXX	49	10:13:39	0.93	134	0.0116	0.75	7.16
	E6	6E4XXXX	53	10:19:25	0.71	202	0.0008	0.16	0.46
	E6	PMXXXX	53	10:24:10	0.68	142	0.0030	0.63	1.84
	E6	SCXXXX	43	10:29:56	0.65	171	0.0015	0.25	0.91
	E5	ADXXXX	29	10:39:28	1.05	106	0.0085	0.62	5.25
	E6	B1XXXX	39	10:55:00	0.96	145	0.0029	0.37	1.80
	E5	BHXXXX	43.5	10:58:21	5.11	221	0.0219	0.91	13.46
	E6	6ZXXXX	46	10:59:18	1.8	213	0.0021	0.07	1.28
JUNE 6 PM	E6	BHXXXX	53.2	12:27:22	3.64	166	0.0192	0.61	11.82
	E6	SKXXXX	52	12:32:43	0.57	157	0.0014	0.21	0.88
	E6	SEXXXX	47	12:33:47	0.8	143	0.0002	0.01	0.13
	E6	VEXXXX	42	12:39:08	1.33	159	0.0009	0.01	0.58
	E6	9BXXXX	37.5	12:41:58	1.57	138	0.0032	0.24	1.94
	E6	SKXXXX	30.5	12:49:54	3.92	366	0.0111	0.94	6.84
	E5	34XXXX	32.5	12:51:33	1.67	282	0.0049	0.66	2.98
	E6	NZXXXX	41	12:56:24	0.83	164	0.0036	0.43	2.19
	E6	JEXXXX	46	12:59:16	0.77	90	0.0033	0.39	2.00
	E6	QAXXXX	46	13:00:47	0.83	241	0.0004	0.07	0.26
	E5	H8XXXX	54.5	13:06:07	1.11	137	0.0047	0.55	2.87
	E6	2SXXXX	52	13:20:19	0.64	349	0.0003	0.04	0.20
	E3	4AXXXX	49.5	13:28:41	2.07	321	0.0050	1.00	3.04
	E4	4ZXXXX	41	13:35:40	2.05	173	0.0053	0.58	3.25
	E5	WAXXXX	38	13:38:23	1.21	106	0.0032	0.36	1.97
	E6	ARXXXX	30.5	13:47:19	1.16	349	0.0010	0.53	0.62
	E6	MMXXXX	31	13:48:27	0.72	152	0.0009	0.07	0.55
	E6	1SXXXX	39	13:52:54	0.53	100	0.0002	0.01	0.15
	E6	5JXXXX	45.5	13:56:12	1.25	128	0.0098	0.84	6.04
	E6	1BXXXX	47.5	13:57:35	0.94	361	0.0013	0.28	0.80
	E6	PBXXXX	49	13:58:40	1.75	308	0.0039	0.93	2.37
	E6	4ZXXXX	55	14:02:28	0.67	170	0.0006	0.03	0.37
	E6	T6XXXX	45	14:16:00	0.56	136	0.0011	0.05	0.68
	E6	EZXXXX	44	14:58:07	0.79	187	0.0036	0.46	2.22
	E6	GBXXXX	38	15:01:30	0.64	205	0.0005	0.05	0.29
	E6	KWXXXX	45	08:58:08	0.73	122	0.0011	0.06	0.69
	E6	TT9XXXX	47	08:59:43	0.67	221	0.0006	0.02	0.35
	E6	4K1XXXX	54	09:04:51	0.67	165	0.0017	0.08	1.02

JUNE 7 AM	E6	1B4XXXX	52	09:09:57	0.94	119	0.0016	0.14	0.98
	E6	2SVXXXX	49	09:11:40	1.49	303	0.0007	0.04	0.43
	E5	B6XXXX	43	09:16:05	4.76	166	0.0199	0.72	12.21
	E3	5A9XXXX	35	09:20:04	1.84	66	0.0245	0.57	15.08
	E6	AR3XXXX	31	09:29:20	1.21	339	0.0022	0.47	1.35
	E5	BH1XXXX	32	09:30:33	2.67	443	0.0055	0.87	3.41
	E5	MS4XXXX	40	09:36:05	1.96	273	0.0049	0.88	3.01
	E5	4E2XXXX	45	09:39:31	1.61	188	0.0066	0.81	4.08
	E5	4Z5XXXX	48	09:41:53	2.19	286	0.0038	0.63	2.33
	E6	TN4XXXX	53	09:45:36	0.69	228	-0.0002	0.00	1.35
	E5	31DXXXX	52	09:53:19	1.75	193	-0.0029	0.07	2.32
	E5	V80XXXX	51	09:54:56	1.97	197	0.0030	0.66	1.84
	E5	31FXXXX	43	09:59:43	2.08	244	0.0037	0.72	2.29
	E3	BB4XXXX	36	10:04:59	1.23	97	0.0162	0.76	9.93
	E6	SA2XXXX	31	10:12:42	1.27	183	0.0054	0.78	3.30
	E6	WL4XXXX	41	10:18:18	1.41	115	0.0057	0.61	3.51
	E6	RJXXXX	46	10:21:54	0.88	123	0.0000	0.00	0.02
	E6	NPOXXXX	48	10:23:45	3.01	150	0.0178	0.92	10.95
	E6	RDXXXX	54	10:27:37	1.34	301	0.0064	0.81	3.94
	E6	WGMXXXX	52	10:35:24	0.75	214	0.0004	0.01	0.23
	E6	8U9XXXX	50	10:44:34	1.39	149	0.0007	0.05	0.43
	E6	EW1XXXX	42	10:46:01	1.27	286	0.0022	0.38	1.33
	E4	4J2XXXX	37	10:48:29	2.44	156	0.0127	0.90	7.78
	E5	VL1XXXX	31	10:58:38	4.34	226	0.0191	0.98	11.74
	E6	BH0XXXX	40	11:04:07	1	92	0.0044	0.14	2.71
	E5	E7XXXX	46	11:09:57	4.03	177	0.0175	0.88	10.77
JUNE 7 PM	E6	BB2XXXX	43	12:35:50	1.41	136	0.0073	0.72	4.52
	E3	TPBXXXX	38	12:39:29	2.12	114	0.0155	0.88	9.55
	E5	RDXXXX	30	12:46:32	1.83	246	0.0074	0.82	4.52
	E5	ONXXXX	32	12:47:37	0.87	122	0.0036	0.38	2.21
	E5	BG6XXXX	33	12:49:21	1.14	57	0.0186	0.64	11.41
	E5	PP8XXXX	40	12:53:05	0.78	110	0.0025	0.36	1.53
	E6	1BXXXX	45	12:56:42	0.77	148	0.0014	0.09	0.84
	E6	1BZXXXX	47	12:58:13	0.64	117	0.0021	0.27	1.26
	E6	5M6XXXX	54	13:02:02	0.86	159	0.0019	0.31	1.14
	E	6ALXXXX	52	13:08:36	3.43	151	0.0199	0.94	12.26
	E6	5P6XXXX	43	13:14:10	0.95	85	0.0029	0.59	1.77
	E2	8S2XXXX	38	13:17:33	3.79	186	0.0169	0.90	10.40
	E6	1BRXXXX	29	13:31:37	0.69	309	0.0009	0.27	0.55
	E6	PO7XXXX	40	13:34:27	0.7	120	0.0008	0.17	0.51
	E6	6T9XXXX	45	13:42:31	1.78	130	0.0080	0.69	4.89
	E6	5Z6XXXX	47	13:44:32	0.79	147	0.0016	0.14	0.98
	E4	PAXXXX	55	13:49:00	1.6	179	0.0046	0.81	2.83
	E	6AEXXXX	52	13:55:56	0.81	216	-0.0008	0.02	2.30
	E6	5AMXXXX	49	13:57:37	0.69	295	0.0003	0.04	0.17
	E6	NS3XXXX	38	14:05:42	0.7	168	0.0010	0.04	0.58

	E4	DS9XXXX	30	14:13:43	2.45	272	0.0083	0.91	5.12
	E5	CECXXXX	32	14:15:01	0.72	151	0.0021	0.26	1.29
	E6	AR1XXXX	40	14:20:27	1.09	303	0.0019	0.51	1.15

Table 6. 1 Summary of vehicles measured with their Euro Standards and concentration of NO Emissions

NO/CO_2 ratio was calculated at the first and then concentration of NO was calculated in grams per Kilowatt-hours (g/kWh) which was included in the final tabular column.

Euro Standards	Vehicle Details	D1 (KM) HIGHWAY	TIME	NO (ppm) average	CO_2 (ppm) average	NO/CO_2 (linear regression)	R^2	NO g/kWh
E5	BH 3XXXX	42	13:11:56	2.76	127	0.013	0.86	8.43
E5	BH 3XXXX	42	13:12:15	3.73	175	0.018	0.99	11.30
E5	NP0XXXX	33	13:26:44	1.32	104	0.006	0.96	4.13
E5	NP0XXXX	33	13:27:16	1.43	135	0.006	0.94	4.25
E6	PA33XXXX	31	14:07:46	0.99	268	0.003	0.96	2.37
E6	PA33XXXX	31	14:07:59	1.04	399	0.001	0.67	1.04
E6	PA33XXXX	31	14:09:38	0.70	302	0.002	0.81	1.74
E5	4J2XXXX	40	14:16:47	1.50	189	0.004	0.68	2.87
E5	4J2XXXX	40	14:17:31	1.52	162	0.007	0.87	4.57
E5	AT31XXXX	26.5	14:44:17	2.12	126	0.009	0.95	5.86
E5	AT31XXXX	26.5	14:45:22	3.40	208	0.012	0.92	7.86
E5	AT31XXXX	26.5	14:46:07	2.29	142	0.012	0.93	7.43

Table 6. 2 Summary of highlighted repeated vehicle details from Table 6.1

The *Table 6.2* shows the highlighted section from *Table 6.1* which gives the test to test repeatability. From the table, it looks like the measurements were repeated multiple times. But the measurements were taken only once in a stretch. This is done in order to show a better correlation by individual events and NO/CO_2 ratio are comparable between tests.

The *Figure 6.1* clearly indicates the percentage of vehicles measured during this experimental campaign with their corresponding Euro Standards. Out of 235 trucks measured, majority of the trucks chased during our study were Euro 6 which contributed around 66%, around 24% were Euro 5, around 3% were Euro 4, around 4% were Euro 3, 1% was Euro 2 and remaining 2% of the measured trucks were not known as the vehicle number were not clear in some of the trucks chased and in some other trucks, Euro Standards obtained were not certain.

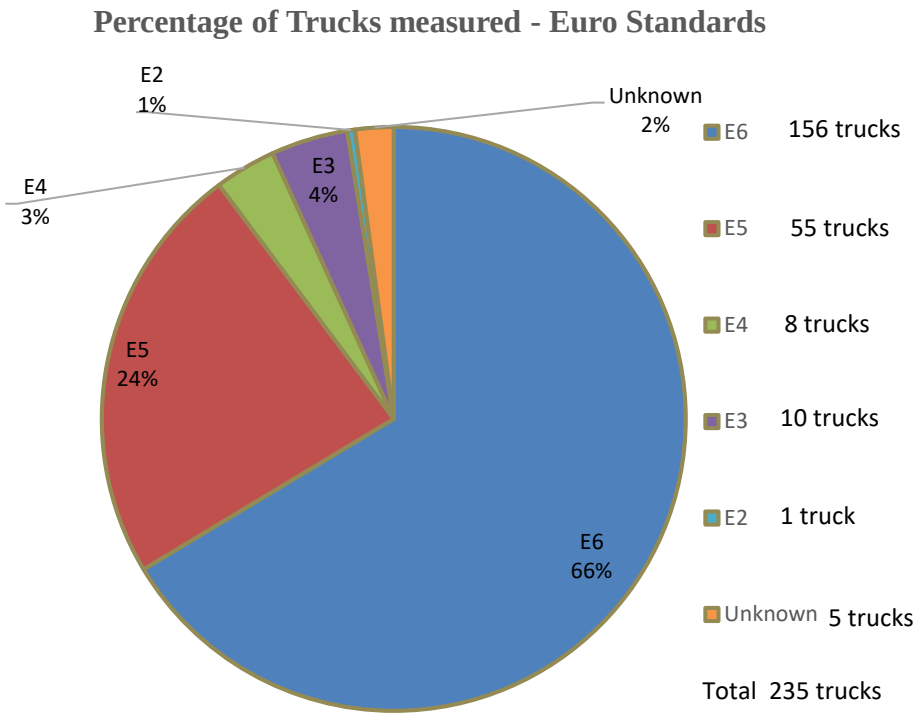

Fig 6. 1 Measured Heavy-Duty vehicles with their Euro Standards

6.2 Area covered during the measurement

This experiment was conducted for a week in a small city named Benešov, in the vicinity of Prague early in the Summer 2019. The goal is to identify tampering, high NO_x tampering where cooling is minimized by running engine in high load and maintaining the SCR in warm condition.

The area shown in *Figure 6.*2 was selected as it has less traffic compared to main cities like Prague. The experimental measurement is conducted in this area as this vehicle chase study would be more efficient in highway. In congested or traffic cities, movement of lot of vehicles in simultaneous time would increase uncertainty in the measurement which would be very hard to predict the exact high emitters. Though high pollution can be found in traffic and urban cities than in highway as SCR performance is less efficient in low speed and high traffic zone, but the performance of SCR and DPF can be improved by additional heating device which would decrease the excess emissions and improves the air quality in concerning environment and human health. The Start and End point mentioned in the map shown in

Figure 6.2 means that the measurements happened in both the direction (start to end point and end to start point) of D1 highway.

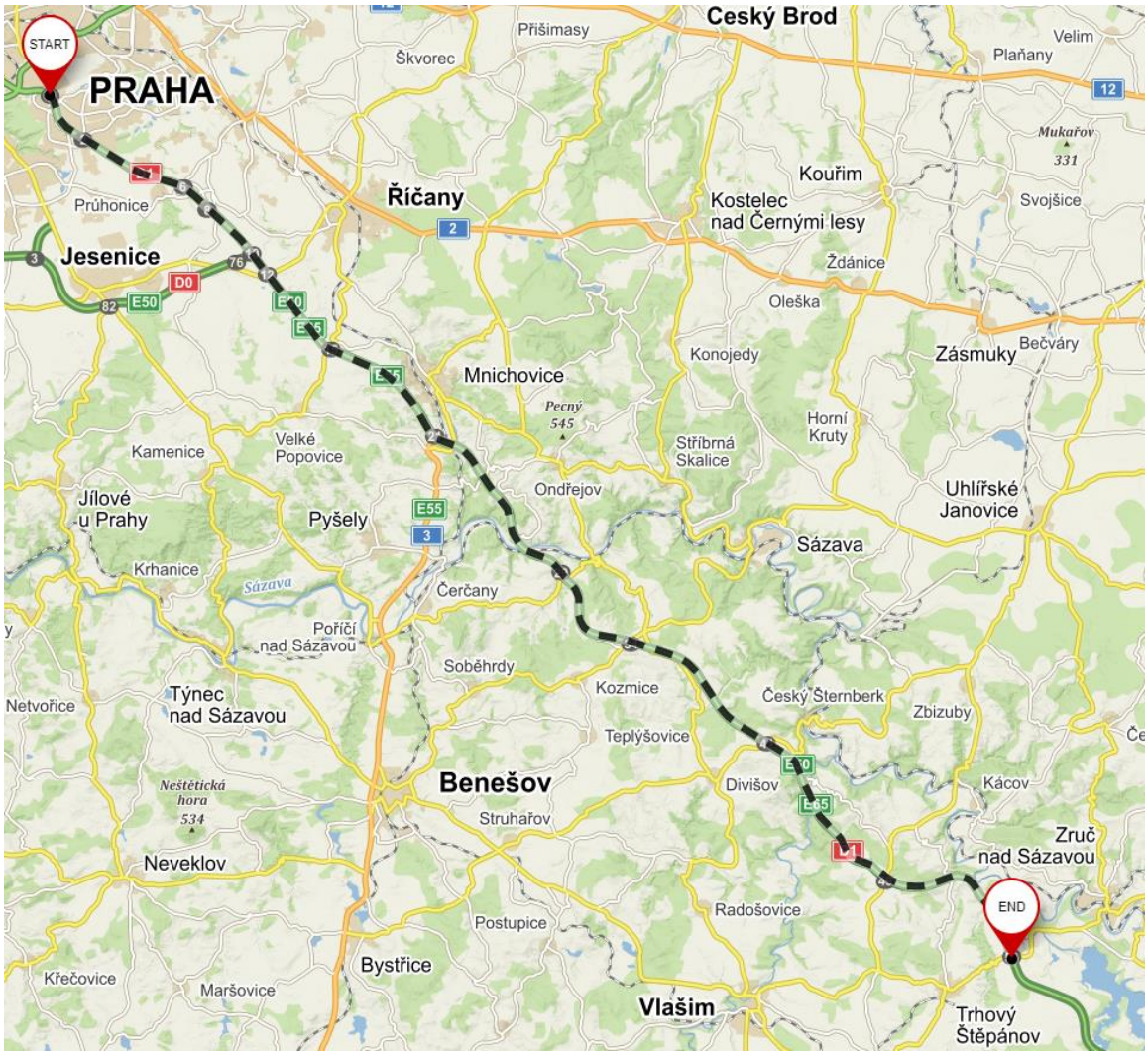

Fig 6. 2 Area of D1 highway covered for measurement of excess emitters [42]

6.3 Road profile

Emissions from the vehicle are possibly not only due to tampering of some after treatment devices, but can be also possible due to driver's behaviour, profile of the road and so on. The experiment was carried out in both the directions of D1 highway.

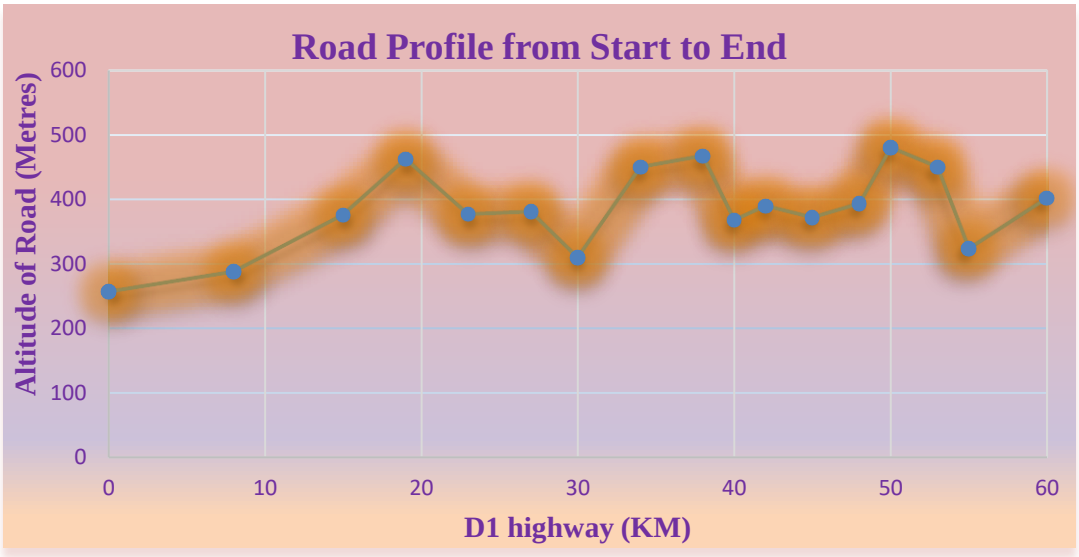

Fig 6. 3 Road profile of covered distance for measurements

The elevation profile of the road covered for our measurements and study had a maximum attitude of 490 metres and minimum altitude of 270 metres above the sea level which is shown in the above *figure 6.3*. The road profile was identified by the covered area during the measurement in the D1 motorway kilometres and they were plotted by the help of Czech website *mapy.cz* which gave the altitude of the road. This road profile was generated in order to find whether they are responsible for high emitters.

6.4 Road profile showing the captured trucks

The road profile mentioned in the *figure 6.3* is smooth and not sharp as shown. Though there was a difference of 220 metres in altitude, it doesn't have a direct rise or fall in profile, but with multiple steps of rise and fall. This means the fall in road profile from higher altitude to lower altitude will not have significant cooling effects and inefficient working of SCR and DPF. But still quite a high NO_x concentration was found from the vehicle mostly at the downgrade of the road which is very strange though that's not a big fall in gradient. The main reason for these can't be predicted for surety unless and otherwise it was noted by some On Board Diagnostic (OBD) or some special camera which tracks driver's attributes during the drive, but possibly it may be due to cooling of SCR and low engine load which decreases the effective functioning as Oxides of Nitrogen that requires certain operating temperature needed for Urea decomposition.

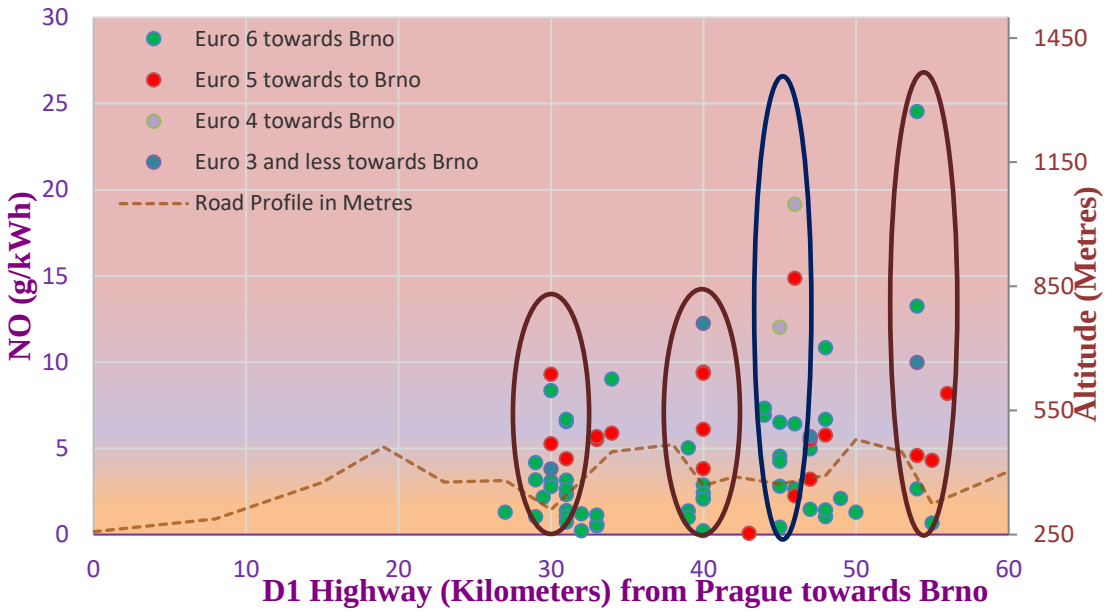

Fig 6. 4 Trucks chased towards the direction of Brno for about 55 kilometres.

The *figure 6.4* shows the measured trucks with the road elevation profile in the direction towards Brno in D1 highway and from the above graph we've quite a lot of trucks which were chased resulted in higher concentration of NO. The three brown circles from the graph shows a down slope of the road in which the trucks measured in this region had significant concentration of NO. These high emitters which were described in the previous chapter could be due to ineffective function of SCR in which the exhaust gas would have been cooled and this results in poor conversion efficiency of Catalytic converter which converts oxides of Nitrogen to Nitrogen. The blue circle also denotes some excess NO_x emitting trucks, but the road profile in this area is almost straight with a negligible down slope.

The *figure 6.5* shows the measured trucks with the road elevation profile in the direction towards Prague in D1 highway. The brown circle denotes the excess amount of NO concentration which was measured in a small downgrade of road where one of the possibilities is that sufficient temperature is not obtained for the effective performance of after treatment system at that instant or some poor maintenance and tampering. The blue circle shows some excess emitters in which all the European Standards of trucks plays a major role irrespective of negligible down slope (gradient) of road profile.

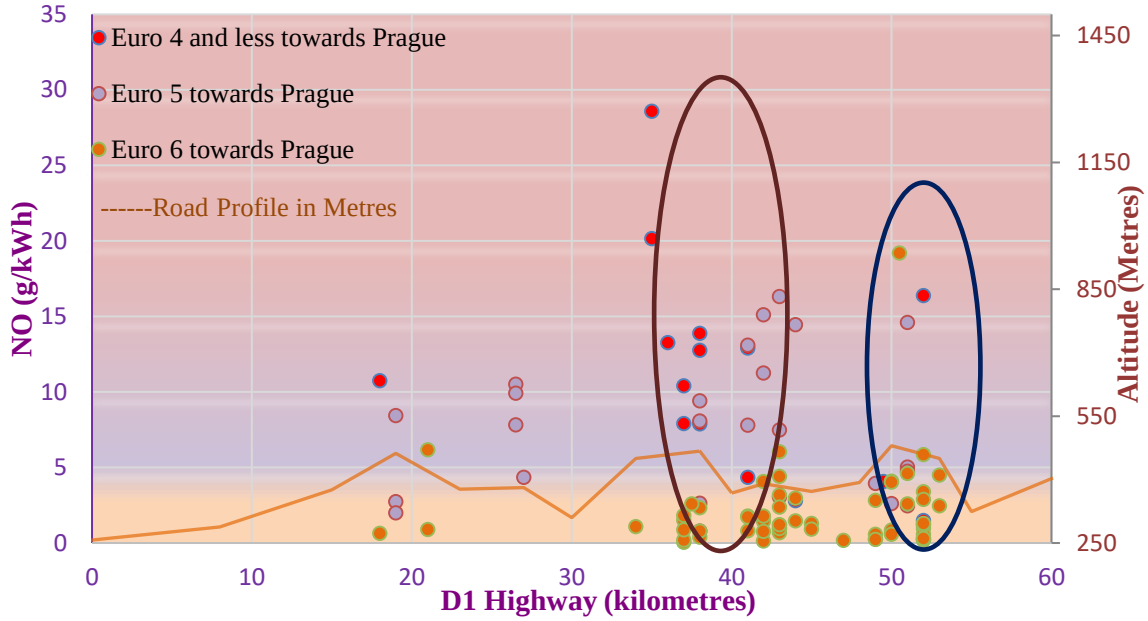

Fig 6. 5 Trucks chased towards the direction of Prague

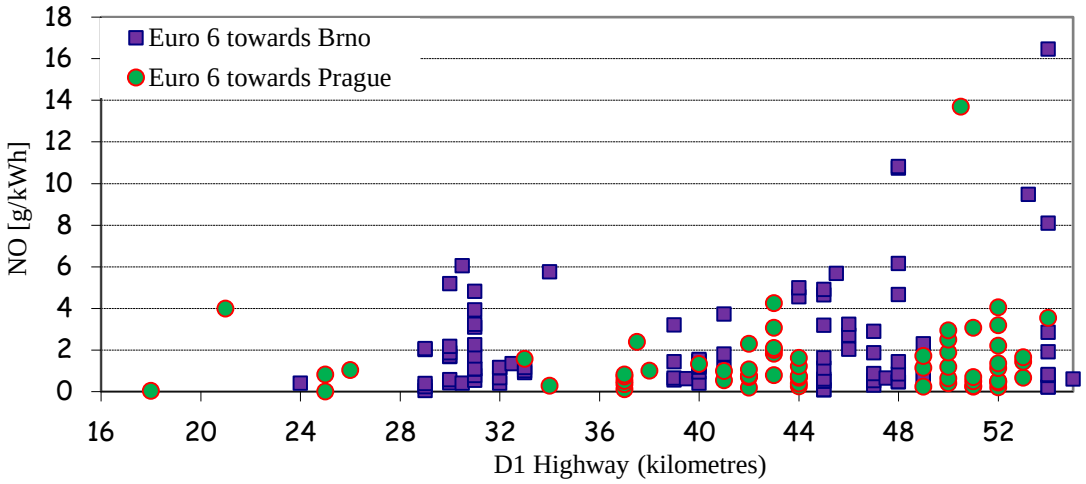

Fig 6. 6 Euro 6 Trucks chased towards in both the direction of Prague and Brno

Figure 6.6 shows the chasing of Euro 6 Trucks in both the directions of Prague and Brno. An interesting fact noted from *Figure 6.6* is that most of the Euro 6 trucks resulted in excess NO_x emitters in the direction of Prague to Brno when compared to the trucks which were travelling in the direction of Brno to Prague. One of the possible reasons is that the legislation is not strictly followed, and so lot of trucks may possibly use some tampering and manipulation devices which results in emitting excess NO_x. In order to protect the environment and human health, the legislation provided should be strictly followed and all the tampering devices must be avoided.

7 Conclusion

The main target of this work was to analyze the data from the experimental campaign focused on NO emissions. The concentrations were measured by FTIR installed in a van. The 'Vehicle Chase method' used in this experimental campaign is one of the interesting methods to measure the exhaust gas of vehicles in real drive and on road. This measurement campaign started from a small city called Benešov and this happened early in Summer 2019 for a week from 3rd of June to 7th of June 2019 in D1 highway connecting Prague and Brno.

Initially, the data obtained from the measurement were considered and for further analysis, the background noise and unwanted signals were differentiated. To differentiate these unwanted noises, baseline was created first, and the detection limit of CO_2 was created. Detection limit was calculated as the product of 3.3 times the standard deviation of background response of measurement before the concentration is detected. Any concentration which are measured above this detection limit are the useful concentration detected to analyze in this work. Detection limit of NO and CO_2 was calculated as 0.78 and 52 ppm. The detected response above this detection limit were analyzed by three different approaches to calculate NO/CO_2 ratio.

The NO/CO_2 ratio were calculated by linear regression approach, Numerical Integration of Area through Peak Area approach and Ratio of maximum point of concentration approach. All these approaches were compared in order to find consistency between them in evaluating NO/CO_2 ratio from the data for analysis. To be detailed, the vehicle with registration number 3Z1XXXX and Euro 4 had a very good correlation and the NO/CO_2 ratio was found to be 0.035, 0.035 and 0.034 by peak area approach, maximum point of concentration of NO/CO_2 and linear regression approach. This had a very good consistency and this truck was found to have a high NO Emission factor of 21.39 g/kWh as detailed in *Table 5.5*.

The approaches were compared with the measured data to get the Emission factor. The results were evaluated and summarized to detect excess NO emission irrespective to their Euro Standards. From this measurement and analysis, most of the high Emission factor was found to have consistent NO/CO_2 ratio when compared between these approaches.

Discussion and Suggestion

The data were collected from the measurement during the experimental campaign which was obtained from Fourier Transform Infrared Spectroscopy with a fast response gas analyzer. The measured data were analyzed. NO/CO_2 ratio was calculated by three different approaches. They are Linear regression, peak area approach and maximum point of concentration in the regime. The maximum concentration and peak area approach to calculate NO to CO_2 ratios are possibly better than linear regression approach because regression approach resulted in negative Emission ratio when there is poor correlation or negative slope. As Emission ratio is only positive value (can't be negative), so area approach is the best approach to get accurate concentration of NO.

High Emitters gained consistent NO/CO_2 ratio from all the three approaches as the higher correlation corresponds to consistent value of NO to CO_2 ratio. Also, excess concentration of NO was measured from all vehicle standards which can be due to some effective performance of tampering devices which were installed by vehicle manufacturers or by some smart technician, manipulation device and improper maintenance of the vehicle or due to ineffective performance of NO_x after treatment devices or there was no after treatment devices installed. This also creates a question regarding the legislation whether it's strictly followed or just an announcement of Emission norms. So, the RDE should be strictly followed by the government in order to protect human health and environment. In addition to this, emissions measured in the test bench is quiet less compared to the measurement in the real drive which may be due to different operating conditions, traffic and diluted gases from the previous vehicles in the air. So, conformity factor plays a major role in this case and nowadays, researches are trying to bring the conformity factor to 1 which means emission during testing in the bench and RDE are equal. This is very hard to achieve.

Further, inspection should be done over a period to follow the Standard limits and those who drive should care their own vehicle by periodical maintenance and service which would also support everyone by giving clean emissions which would reduce air pollution in protecting human health and environment.

Also, aftertreatment devices play a major role in converting the harmful emissions to harmless emissions. Exhaust Gas Recirculation (EGR) is a very important technique to reduce the harmful emission of NO_x. This is done to reduce the peak in-cylinder temperature which were resulting in enormous concentration of Oxides of Nitrogen. Cooling of SCR is a natural process which varies from operating conditions but still reducing the heat transfer between the exhaust gas to the atmosphere through conduction and convection in exhaust manifold would result in effective performance of SCR. Possibly SCR emulators play a major role for these harmful emissions. They should be well educated as these tampering methods have no increase in fuel usage, but indirectly causes other health and environmental issues which causes respiratory diseases or destroy other beings in the environment.

In addition to this, from the *figure 6.6,* most of the Euro 6 trucks which were leaving Prague towards the direction of Brno were resulting in excess concentration of NO_x. One of the possibilities is that manipulation devices and tampering devices would have been turned on which results in poor performance of after treatment devices. So, an effective and strict legislation should be followed in real drive measurement for healthy life and saving the environment from harmful gases. During these measurements, some vehicles had a lower concentration of NO at some period and the same vehicle had a high concentration which were described as inconsistent emitters. This results in uncertainty in the measurement. Detection limit was calculated by taking the standard deviation of background and multiplied by 3.3 to measure the useful concentration. This seems to be a better method for calculating detection limit. High concentration of NO measured from a vehicle can't be judged as high emitting trucks unless and otherwise they are measured for a whole WLTC, as possibly high concentration was seen during the short measurement and maybe it can have less concentration during the other period. Portion of the vehicle registration number is excluded for personal data protection reasons and its denoted as XXXX. Though NO_x comprises NO, NO_2 and so on, in this measurement the concentration of NO was detected and analysed, and the Emission factor of NO was calculated. Emission factor of NO_x can be higher than Emission factor of NO if there is a presence of NO_2. But NO_x concentration can never attain concentration lower than detected NO in this measurement.

References

[1] Manjula R. Canagaratna, John T. Jayne, David A. Ghertner, Scott Herndon, Quan Shi, Jose L. Jimenez, Philip J. Silva, Paul Williams, Thomas Lanni, Frank Drewnick, Kenneth L. Demerjian, Charles E. Kolb & Douglas R. Worsnop, "Chase Studies of Particulate Emissions from in-use New York City Vehicles," *Aerosol Science and Technology*, vol. 38, no. 6, pp. 555-573, 24 June 2010.

[2] López-Martínez, J.M., Jiménez, F., Páez-Ayuso, F.J., Flores-Holgado, M.N., Arenas, A.N., Arenas-Ramirez, B., & Aparicio-Izquierdo, "Modelling the fuel consumption and pollutant emissions of the urban bus fleet of the city of Madrid," *ScienceDirect* , vol. 52, pp. 112-127, 2017.

[3] L. European Environment Agency - Moosmann, M. Tista, S. Haider, M. Gager, S. Schindlbacher and E. Kampel, "Environmental degradation, Environment policy and protection of the environment," European Union emission inventory report 1990–2011 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), 27/06/2013. https://op.europa.eu/cs/publication-detail/-/publication/6f0b4522-d350-42bb-867a-519611d99b65

[4] Zavala, M., Herndon, S. C., Wood, E. C., Jayne, J. T., Nelson, D. D., Trimborn, A. M., Dunlea, E., Knighton, W. B., Mendoza, A., Allen, D. T., Kolb, C. E., Molina, M. J., and Molina, L., "Comparison of emissions from on-road sources using a mobile laboratory under various driving and operational sampling modes," *Atmos. Chem. Phys*, p. 1–14, 2009.

[5] "The National Pollutant Inventory (NPI)," Department of the Environment and Energy, Australian Government, 10 August 2018. http://www.npi.gov.au/

[6] Avinash kumar Agrawal, Shrawan Kumar Singh, Shailendra Sinha, Mritunjay Kumar Shukla, "Effect of EGR on the exhaust gas temperature and exhaust opacity in

compression ignition engines," *Research Gate*, vol. 29, no. 3, pp. 1-2, pp.275-284, June 2004.

[7] "Air Quality in Europe," European Environment Agency, 29 October 2019. https://www.eea.europa.eu/publications/air-quality-in-europe-2019

[8] G. S. Hebbar, "NOx from Diesel Engine Emission and Control Strategies," *International Journal of Mechanical Engineering and Robotics Research (IJMERR)*, vol. 3, p. 472, 2014.

[9] J. B. Heywood, Internal Combustion Engine Fundamentals, New York: McGraw-Hill, Inc., 1988.

[10] R. Stone, Introduction to Internal Combustion Engines, London: MACMILLAN, 1985.

[11] O. Vítek, "Theory Of Internal Combustion Engine," Prague, https://studium.fs.cvut.cz/studium/u12120/MAE/, 2017.

[12] Prof. Dr. Olaf Deutschmann, K. Hauff, U. Nieken, Universität Stuttgart, "Chemical Technology," *Karlsruhe Institute of Technology (KIT) Research.*

[13] PhD Student Eng. Vrabie V., Prof. Dr. Eng. Scarpete D., PhD Student Eng. Zbarcea O, "The New Exhaust after treatment system for reducing NOX," *ISSN 1310-3946 - International Scientific - Technical Conference "trans & MOTAUTO '16",* vol. 1, no., pp. 110-113, 2016.

[14] J. Rocha, "Clean Diesel," *Diesel Technology Forum*, pp. 1-3, 24 9 2019. https://www.dieselforum.org/news-and-resources/policy-insider/cleaner-fuels-cleaner-engines/clean-fuel-ultra-low-sulfur-diesel//cleaner-fuels-cleaner-engines/clean-fuel-ultra-low-sulfur-diesel

[15] B. Scott Jackson, "DEF Market- Pumps & Systems," Google Image Result for https://www.pumpsandsystems.com/sites/default/files/Blackmer-SCR-process.jpg.. https://www.google.com/imgres?imgurl=https%3A%2F%2Fwww.pumpsandsystems.com%2Fsites%2Fdefault%2Ffiles%2FBlackmer-SCR-process., 2012.

[16] Michal Vojtíšek,Center for Vehicles for Sustainable Mobility, Czech Technical University in Prague, "Overview of pollutants of concern and their production.," Prague, 2017-2018. https://studium.fs.cvut.cz/studium/u12120/MAE/, 2017

Czech National Inst. Of Health 2013 –7-8 thousands annually in CZ http://apps.szu.cz/svi/hygiena/archiv/h2013-1-02-full.pdf

WHO: 7 million annually worldwide (25.3.2014) http://www.who.int/mediacentre/news/releases/2014/air-pollution/en/

[17] Yves Chauvin, Robert H Grubbs, Richard R Schrock, Environmental Chemistry, NCERT: 11083CH14, 2019.

[18] Janez Potočnik, "Air Pollution and Our need to Reduce it," EU Commissioner for the Environment https://ec.europa.eu/commission/presscorner/detail/en/SPEECH_12_635

[19] Maroa Semakula, Prof Freddie Inambao, "The Formation, Effects and Control of Oxides of Nitrogen in Diesel Engines," *International Journal of Applied Engineering Research*, vol. 13, no. 0973-4562, pp. 3200-3209, (2018).

[20] B. Governor, "Bangkok post," Online Reporters, Bangkok, 2019. https://www.bangkokpost.com/thailand/general/1762679/polluting-vehicles-to-be-ordered-off-city-roads

[21] W. H. Organization, "Ambient air pollution: A global assessment of exposure and burden of disease," ISBN: 9789241511353, 2016. https://www.who.int/phe/publications/air-pollution-global-assessment/en/

[22] Air Quality in Europe, "Air Pollution, Environment and Health," European Environment Agency (EEA), 16 October 2019. https://www.eea.europa.eu/publications/air-quality-in-europe-2019

[23] Dieselnet, "Emission Standards," Diesel Net, 07 2019. [Online]. Available: [Accessed 30 10 2019]. www.dieselnet.com/standards/eu/hd.php.

[24] A. Krajinska, Transport & Environment, "EURO 7: The Final Emission Roadmap," in *Path towards EURO 7*, Stuttgart, 21 May 2019.

[25] CITA, Tampering of Emission control System, "UNECE Transport (GRPE-78-04), Agenda 4a," 8-11 January 2019. [Online]. Available: [Accessed 31 10 2019]. www.unece.org/trans/main/wp29/wp29wgs/wp29grpe/grpeinf78.html.

[26] Karl Ropkins Institute for Transport Studies, University of Leeds, "Real-World Vehicle Exhaust Emissions Monitoring: Review and Critical Discussion," *Critical reviews in Environmental Science and Technology,* vol. 39, no. 2, pp. 79-152, 2009.

[27] Janet Yanowitz Michael S. Graboski, Lisa B. A. Ryan, Teresa L. Alleman and Robert L. McCormick, "Chassis Dynamometer Study of Emissions from 21 In-use Heavy-Duty Diesel Vehicles," *Environmental Science and Technology 1999, 33, 2, 209-216,* 3 December 1998.

[28] Thomas W. Kirchstetter, Robert A. Harley, Nathan M. Kreisberg, Mark R Stolzenburg, Susanne V. Hering, "On-road measurement of "fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles," *Atmospheric Environment,* vol. 33, no. 18, pp. 2955-2968, 8 January August 1, 1999.

[29] Gary A. Bishop, Morris JA, Stedman DH, Cohen LH, Countess RJ, Countess SJ, Maly P, Scherer S., "The Effects of Altitude on Heavy-Duty Diesel Truck On-Road Emissions," *Envronmental Science and Technology,* vol. 25, no. 8, pp. 1574-1578, 2001.

[30] Y. Suresh, "Detection of High Particle Emitters," CVUT Diplomova Prace, Prague, 2018.

[31] Dr Ing Bastian Holderbaum, Dipl Ing Michael Kind, FEV Gmbh, Aachen, FEV Italia, "Potential for Euro 6 Passenger Cars with SCR to meet RDE Requirements," *AECC* , vol. 36, no. Internationales Wiener Motorensymposium , pp. 1-2, 2015.

[32] Denis Pöhler, Tim Adler, Christopher Krufczik, Martin Horbanzki, Johannes Lampel and Ulrich Platt, University Of Heidelberg, Institue of Environmental Physics, Heidelberg, Germany (denis.poehler@iup.uni-heidelberg.de), "Real Driving NOx Emissions of European Trucks and Detection of Manipulated Emission Systems," *European Geosciences Union Assembly* , vol. 19, no. EGU2017-13991-1, p. 1, 2017.

[33] N. Verma, "Research and Development, IIT Kanpur," Department of Chemical Engineering,Core Lab 201D, 2012. [Online]. Available:. [Accessed 2019]. https://www.iitk.ac.in/dordold/index.php?option=com_content&view=category&layout=blog&id=221&Itemid=240

[34] B. Optics, "Innovation with Integrity - FT-IR," Bruker, [Online]. Available: [Accessed 11 October 2019]. https://www.bruker.com/fileadmin/user_upload/8-PDF-Docs/OpticalSpectrospcopy/Gas_Analysis/MATRIX-MG/Brochures/MATRIX_MG_Brochure_EN.pdf.

[35] Martin Pechout,Martin Kotek,Petr Jindra,David Macoun,Jan Hart and Michal Vojtisek, "Comparison of hydrogenated vegetable oil and biodiesel effects on combustion, unregulated and regulated gaseous pollutants and DPF regeneration procedure in a Euro6 car," *Science of the total Environment,* p. 14, 2019.

[36] J. Vavra, "Data Acquisition," CVUT, 2017. [Online]. Available: https://studium.fs.cvut.cz/studium/u12120/MAE/, 2017 [Accessed 12 November 2019].

[37] Lea G. Johnsen, Thomas Skov, Ulf Houlberg and Rasmus Bro, "An automated method for baseline correction, peak finding and peak grouping in chromatographic data," *Analyst*, vol. 3502, p. 138, 2013. https://www.researchgate.net/publication/236691536

[38] Greg Wells, Harry Prest, and Charles William Russ IV, Agilent Technologies,2850 Centerville Road, Wilmington, DE 19809-1610, "Signal, Noise, and Detection Limits in Mass Spectrometry," Agilent technologies- Technical Report-5990-7651EN, USA, April 28, 2011.

[39] E. Theodorsson, "Limit of detection, limit of quantification and limit of blank," EFLM, 2014.

[40] I. Ježek, T. Katrašnik, D. Westerdahl and G. Močnik, "Black carbon, particle number concentration and nitrogen oxide emission factors of random in-use vehicles measured with the on-road chasing method," *Atmospheric Chemistry and Physics- European Geoscience union,* vol. 15, no. 19, 05 Oct 2015.

[41] M. Vojtisek, "Personal communication," Prague, 2019.

[42] Mapy.cz, Google, [Online]. Available: https://en.mapy.cz/zakladni?x=14.8501146&y=49.7161439&z=10&source=muni&id=3469. [Accessed 25 11 2019].

Nomenclature

$BaCO_3$	Barium Carbonate
BS	Bharath Stage (Indian Standards)
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DEF	Diesel Exhaust Fluid
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
ECE	Urban Driving Cycle
ECU	Electronic Control Unit
EGR	Exhaust Gas Recirculation
ELR	European Load Response
EOBD	External On-Board Diagnostics
ESC	European Stationary Cycle
ETC	European Transient Cycle
EU	Europe
FT-IR	Fourier Transform InfraRed
g/kWh	Grams Per Kilo Watt Hour of Power
H_2O	Water
HC	Hydrocarbon
HCCI	Homogeneous Charge Compression Ignition
HCLI	Homogeneous Charge Late Injection
HO_2	Hydroperoxyl protonated form of superoxide
HPLI	Highly Premixed Late Injection
IDL	Instrument Detection Limit
LNT	Lean NO_x trap
LOD	Limit of detection
LTC	Low Temperature Combustion
MDL	Method Detection Limit
N	Monoatomic Nitrogen

N_2	Molecular Nitrogen (Diatomic)
NH_3	Ammonia
NO	Nitric Oxide
NO/CO_2	Emission ratio or Emission Factor
NO_2	Nitrogen Dioxide
NO_x	Oxides of Nitrogen
O	Atomic Oxygen
O_2	Oxygen
OH	Hydroxide
PCCI	Premixed Charge Compression Ignition
PM	Particulate Matters
PN	Particle Number
Pt	Platinum
R^2	Correlation
RCCI	Reaction Controlled Compression Ignition
RDE	Real Drive Emission
SCR	Selective Catalytic Reduction
SNR	Signal to Noise Ratio
WHO	World Health Organisation
WHSC	World Harmonized Stationary Cycle
WHTC	World Harmonized Transient Cycle
μ	Mean
σ or SD	Standard deviation

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