DEPARTAMENTO DE INGENIERÍA MECÁNICA
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**NO_x emissions from passenger cars under real driving
conditions**

Doctoral thesis

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Como escribió José Ortega y Gasset “Yo soy yo y mis circunstancias”. Luego de tres años de arduo trabajo y dedicación durante el doctorado, sin duda, he crecido en el ámbito profesional, emocional y en la forma de ver el mundo. Las circunstancias que se han dado y las personas que me han rodeado han aportado mucho para dar ese paso hacia adelante en mi vida.

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Las citas textuales pertenecen a El principito, Antoine de Saint-Exupéry

Resumen

La contaminación producida por los vehículos automotores afecta la calidad del aire de las ciudades de todo el mundo. En la conducción en condiciones reales, la mayoría de los turismos diésel Euro 5 y los primeros Euro 6, exceden los límites de emisión de óxidos de nitrógeno (NO_x) reportados en el proceso de homologación. Además, la predicción de las emisiones de NO_x es imprecisa, debido a su no linealidad y su dependencia de la acción del sistema de postratamiento, lo que disminuye la certeza de las estimaciones de NO_x . Estos aspectos restringen la aplicabilidad de políticas para la mitigación de la contaminación.

El objetivo de este trabajo es proporcionar un mejor entendimiento de las condiciones donde se producen las mayores emisiones de NO_x de los turismos, y mejores criterios de cuantificación para los modelos microscópicos de emisiones, en particular, de los vehículos diésel Euro 6 en condiciones reales de conducción. Los vehículos ensayados, tenían diferentes sistemas de propulsión y de postratamiento, que incluían vehículos de gasolina con catalizador de tres vías (*three-way catalyst*, TWC), específicamente, un vehículo de inyección directa de gasolina y un vehículo híbrido eléctrico; cuatro vehículos diésel con recirculación de gases de escape, trampa de NO_x (*lean-burn NO_x trap*, LNT) y reducción catalítica selectiva (*selective catalytic reduction*, SCR). Se realizó un análisis estadístico descriptivo para encontrar la relación entre las emisiones de NO_x y las condiciones de operación del vehículo, del motor y del sistema de postratamiento. Luego, se comparó un modelo de emisiones físico, uno basado en datos, y un modelo híbrido, para comprender la influencia de los picos de emisión NO_x en la predicción de estos modelos microscópicos.

Las altas emisiones instantáneas de NO_x (picos de NO_x), se agruparon utilizando un nuevo método desarrollado, denominado *high emission sets* (HES). Usando HES, los resultados muestran que los picos de NO_x representan un gran porcentaje de las emisiones totales, pero se producen en muy cortos periodos de tiempo. Las emisiones de NO_x se muestran como una función no lineal que depende de las condiciones de funcionamiento del tren motriz, de la inyección de combustible y, en particular, del sistema de reducción de NO_x . De la muestra de vehículos analizados, el vehículo híbrido de gasolina y el diésel con SCR, mostraron emisiones de NO_x en condiciones reales de conducción por debajo de los límites de Euro 6. Se demostró, que la eficiencia de los sistemas TWC y SCR, ambos convertidores catalíticos continuos, depende de las temperaturas de funcionamiento, y en el caso de los TWC, de la relación aire-combustible. Así, durante los primeros cinco minutos de arranque en frío, los niveles de emisión del vehículo híbrido y del diésel con SCR, alcanzaron valores similares a los observados para los equipados con otras tecnologías de control de NO_x . Además, la baja carga en conducción urbana o los descensos en rural enfriaron al SCR, lo que disminuyó su eficiencia. Estos aspectos sugieren la necesidad de un precalentamiento activo para los SCR y TWCs (en aplicaciones híbridas). Por otro lado, los altos niveles de emisiones

de NO_x medidas en el vehículo de inyección directa se presentaron por el continuo funcionamiento en relaciones aire-combustible de mezcla pobre, donde el catalizador TWC disminuye la eficiencia para reducir los NO_x . Con respecto a los modelos de emisión microscópicos, en el caso de los sistemas de reducción catalítica selectiva (SCR), los resultados sugieren la necesidad de modelar las emisiones de NO_x en dos bloques, uno para predecir las NO_x a la salida del motor y otro para las predicciones en el tubo de escape. La baja ocurrencia de los picos de NO_x afecta a la predicción de los factores de emisión. Por otro lado, las "bajas" emisiones de NO_x influyen en las métricas de predicción instantánea como R^2 y RMSE. Los parámetros de la actividad del vehículo se convirtieron en datos de entrada útiles para los modelos basados en la física de los sistemas, y para los modelos de aprendizaje automático. Un enfoque híbrido que combina el modelo basado en la física, con un modelo de aprendizaje automático para el sistema de postratamiento resultó como la mejor alternativa, al usar las ventajas ambos enfoques, reduciendo la cantidad de mediciones y la caracterización del sistema de escape y sus elementos.

Abstract

Pollution from motor vehicles affects air quality in all global cities. In real-world driving, most Euro 5 and early Euro 6 diesel passenger cars exceed the nitrogen oxides (NO_x) emission limits of the type approval procedure. In addition, the prediction of instantaneous NO_x emissions is difficult because of its high nonlinearity and dependence of aftertreatment action, which decreases the certainty of NO_x estimations. These aspects restrict the applicability of policy strategies for the mitigation of pollution.

The objective of this work is to provide a better understanding of motor vehicle NO_x emissions and better quantification criteria for microscopic emission models, in particular, from diesel Euro 6 passenger cars under real-world driving conditions. Therefore, in this study, real-world NO_x emissions and operational data from Euro 6b passenger cars were examined. The vehicles had different powertrains and aftertreatment systems including gasoline vehicles with a three-way catalyst (TWC), namely, one gasoline direct injection (GDI) and one hybrid electric vehicle (HEV); four diesel vehicles with only exhaust gas recirculation (EGR), lean-burn NO_x trap (LNT) and selective catalytic reduction (SCR). Descriptive statistical analysis was performed to determine the relationships between NO_x emissions and the vehicle, engine, and aftertreatment operation conditions. Then, a physical, a data-driven, and a hybrid microscopic model were compared to understand the influence of the NO_x emissions peaks on the prediction accuracy of microscopic models.

High instantaneous NO_x emissions (NO_x peaks) were clustered using a new developed method called high emission sets (HES). The results obtained using HES, indicate that the NO_x peaks account for a large proportion of the total emissions produced in a short amount of time. The NO_x emissions are reflected as a high nonlinear function dependent on the operating conditions of the powertrain, fuel injection, and particularly, of the NO_x control system. From the sample of tested vehicles, the gasoline hybrid electric and diesel SCR-equipped vehicles showed real-world NO_x emissions under Euro 6 limits. It was demonstrated that the efficiency of TWC and SCR systems—both continuous catalytic converters—depend on operating temperatures, and in the case of TWCs, on air-fuel ratios. Therefore, during the first five minutes of cold start, the HEV and SCR-diesel emission levels reached similar values to those observed for the other NO_x control technologies. In addition, low loads in urban driving or downhill in rural areas cooled down the SCR catalyst, thereby decreasing efficiency. These aspects suggest the need for active heating for SCR and TWC (in hybrid applications) aftertreatments. High NO_x emissions were measured from the GDI because of the recurrent leaner air-fuel ratios, where the TWC catalyst decreased the de NO_x efficiency. Regarding microscopic models, in the case of selective catalytic reduction (SCR) systems, the results suggest the need for modelling NO_x emissions in two blocks: one for engine-out outputs and another for tailpipe predictions. The low occurrence of the NO_x peaks affects the accuracy of the predicted emission factors. “Low” NO_x emissions affect instantaneous prediction

metrics, such as R^2 and RMSE. The use of vehicle activity parameters becomes useful inputs to model physics-based, and machine learning models. A hybrid approach that combines the physics-based model with a machine learning model for the aftertreatment system is a good alternative as enables the use of the advantages of the physics and data-driven models for reducing the amount of dimensioning and characterisation of the aftertreatment layout.

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Acronyms and abbreviations

ASC	Ammonia slip catalyst
BTC	Before top centre
CDF	Cumulative density functions
CF	Conformity factor
CI	Compression ignition
CMEM	Comprehensive Modal Emissions Model
CRDI	Common-rail diesel injection
CS	Cold start
DOC	Diesel oxidation catalyst
DPF	Diesel particle filter
DR	Deviation ratio
EEA	European Environment Agency
EF	Emission factor
EFE	Emission factor error
EFM	Exhaust flow meter
EGR	Exhaust gas recirculation
EOV	Externally observable variable
EPA	United States Environmental Protection Agency
GDI	Gasoline direct injection
GHG	Greenhouse gases
HES	High emission set
HEV	Hybrid electric vehicle
HR	Hot running
ICE	Internal combustion engine
INSIA	University Institute of Automobile Research
IOV	Internally observable variables
LES	Low emission set
LNT	Lean-NO _x trap
ML	Machine learning
MOVES	Motor Vehicle Emission Simulator
MSE	Mean square error
NDIR	Non-dispersive infrared
NDUV	Non-dispersive ultraviolet
NEDC	New European driving cycle
NTE	Not-to-exceed
OBD	On-board diagnosis
PDF	Probability density function
PEMS	Portable emissions measurement systems
PFI	Port fuel injection
PHEM	Passenger car & Heavy-duty Emission Model
PM	Particulate matter

PN	Particle number
RDE	Real-driving emissions
RF	Random forests
RMSE	Root-mean-square error
RPA	Relative positive acceleration
RS	Remote sensing
SCR	Selective catalytic reduction
SI	Spark ignition
TUGraz	Graz University of Technology
TWC	Three-way catalyst
UPM	Universidad Politécnica de Madrid
VGT	Variable geometry turbocharger
VSP	Vehicle specific power
VT-micro	Virginia Tech microscopic model
WLTC	Worldwide harmonised light vehicles test cycle
WLTP	Worldwide harmonised light vehicles test procedure

CHAPTER 1

Introduction

1.1. Introduction and problem statement

Since the significant improvement of the steam engine by James Watt in the 18th century, humanity has been using fossil fuels for its industrial and economic growth. In 2017, fossil fuels represented 81 % of the supplied primary energy in Europe (IEA, 2019a). The effects of pollution on the environment and human health are currently widely accepted. As a key actor, the transport sector accounts for one-quarter of CO₂ emissions in Europe (IEA, 2019b), among other greenhouse gases (GHG). The transport sector also generates pollution, where nitrogen oxides (NO_x) emissions are the primary concern to urban air quality and human health.

CO₂ emission levels for the EU fleet-wide average emission of new passenger cars for 2015 was regulated to 130 g km⁻¹. For 2021, this is established to 95 g km⁻¹, which implies a fuel consumption of around of 3.6 and 4.1 L per 100 km for diesel and gasoline vehicles, respectively (EU, 2019). However, CO₂ emission levels are reported on the base of laboratory cycles, and evidence suggests that officially reported CO₂ values do not reflect the actual performance of vehicles on the road. (Fontaras et al., 2017) reported a difference of 30–40 % between official values and real-world estimates.

NO_x emissions affect the air quality of cities and contribute to exceeding the critical loads of eutrophication in Europe (Jonson et al., 2017). During 2013–2015, a large proportion of the urban population (7–9 %) in the European Union (EU) was exposed to NO₂ levels that exceeded the EU limits (Indicator CSI004) and World Health Organization guideline (EEA, 2015). The transport sector was responsible for half of the NO_x emissions and 13 % of other pollutants (EEA, 2017a). For the road transport, this is partially explained by the ‘dieselization’ of the European market, wherein the proportion of diesel vehicles in the passenger car fleet increased from 27 to 41 % between 2005–2015 (EEA, 2017b). This fleet represents 65 % of global diesel vehicles sales (ICCT, 2016).

Variability of real-world NO_x emissions

The key elements that limit pollution from internal combustion engines (ICE) are aftertreatment systems, which have been developed as a consequence of stringent regulations. To limit NO_x emissions in Europe, the European Commission has introduced new type approval procedures since the 90’s. However, the reduction in emissions during the last 20 years has been lower than expected (EEA, 2017a). In part, the problem is that light-duty vehicles were homologated under the new European driving cycle (NEDC) for many years (Carslaw et al., 2011; Hooftman et al., 2018). This cycle does not reflect real-world driving because of insufficient dynamic conditions with long constant

acceleration periods, smooth accelerations, and low speeds (Franco et al., 2013; Ntziachristos et al., 2016). This implies that outside of NEDC conditions, the emissions exceed the type approval limits. In particular, real-world driving NO_x emissions of diesel vehicles Euro 5 and 6 exceed emissions limits (EC, 2016a) substantially. From September 2017, emissions are assessed using the worldwide harmonized light vehicles test cycle (WLTC) and the real-driving emissions (RDE) test using portable emissions measurement systems (PEMS) (EC, 2016b).

The wide variability of NO_x emissions from Euro 6 vehicles has been evidenced by studies of extensive fleets. (Franco et al., 2014; Ntziachristos et al., 2016) determined the actual emission levels of light-duty vehicles using extensive databases collected from several sources. (Yang et al., 2015a) tested 73 Euro 6 diesel vehicles using the WLTC cycle, and (O'Driscoll et al., 2018, 2016) conducted measurements of 39 Euro 6 diesel vehicles in real-world driving conditions with PEMS and with 149 Euro 5 and 6 diesel, gasoline and hybrid vehicles, respectively. These studies identified few vehicles with NO_x emissions under the Euro 6 limit, particularly in the case of diesel passenger cars, with high emitters that exceeded the Euro 6 value by up to 27 times. This is because of the different configurations of the aftertreatment system and NO_x control strategies. Further, most of them were optimised for the NEDC cycle (Yang et al., 2015a). Another possibility is because of the use of improper defeat strategies (Degraeuwe and Weiss, 2017). This implies that the type approval process of NO_x emissions has been ineffective, and does not allow for the generalisation of emissions from the diesel vehicle fleet (Hooftman et al., 2018). Therefore, it is essential to attain a better understanding of how NO_x emissions from Euro 6 vehicles are produced. The effect of their emissions may be mitigated via the implementation of appropriate policies and the appropriate estimation of emission inventories. Millions of these vehicles are driven around the world and Euro regulations have been adopted in Asia, Latin America, and Oceania; therefore, this is not only important to Europe, but for all countries (Ntziachristos et al., 2016).

The problem of NO_x prediction

The effects of vehicle emissions can be quantified more precisely by performing on-road measurements using PEMS to collect vehicle dynamics, engine data, road topography and emissions during real-world operation. However, it is not feasible to measure every vehicle technology and cover all real-driving operating conditions (Duarte et al., 2015). The modelling and prediction of NO_x emissions are important to develop emission inventories and to assess strategies and policies for emission mitigation. However, there currently are difficulties in predicting NO_x emissions and in particular, instantaneous emissions accurately. Although fuel flow rate and CO₂ are positive correlated with power, in most of the cases, the engine-out NO_x emission rates vary monotonically and nonlinearly with positive power (Sandhu and Frey, 2013). For example, under the development of PΔP model, Smit states that this model based on power wheel for Euro 4 vehicle class predicts NO_x emissions poorly with an R² of 0.17 (Smit, 2013). The study stresses that this model is unable to reproduce emission peaks, which makes it difficult to predict instantaneous NO_x emissions from modern vehicles. CO (in gasoline) and NO_x

(in the diesel) vehicles are more complicated to estimate as compared to CO₂ emissions because of the effects of aftertreatment systems. Meanwhile, emission standards have become progressively more stringent since their introduction in 1992, which have largely reduced tailpipe emissions (Hajmohammadi et al., 2019). The actual modelling and understanding of NO_x emissions from Euro 6 cars has become more difficult because of their dependencies on many unknown or estimated parameters related to several systems of the vehicle. The modelling depends on engine type and its control strategies, the behaviour of other aftertreatment elements, and the design or strategy of the NO_x control systems themselves. These aspects decrease the prediction capability of parametric statistical models or simplified physics-based models.

Knowledge of real-world NO_x emissions is useful to improve both micro-emission models and environmental policies. It is relevant to accomplish several sustainable development goals (SDG) presented by the United Nations (UN). In particular, complying in real-world operations with Euro 6 NO_x limits is key to maintain clean air, water, and land, related to SDG 11: Sustainable cities and communities, SDG 14: Life below water, SDG 15: Life on land (Wang and Olsson, 2019), and it must be balanced with the GHG reduction, which is related to SDG 13 that calls on the decrease in climate change by reducing global warming.

1.2. Objectives

In light of the problems identified above, the primary objective of this thesis is to provide a better understanding of motor vehicle NO_x emissions and improving the quantification criteria for microscopic emission models; in particular, from diesel Euro 6 passenger cars under real-world driving conditions. The specific objectives are:

- a) To evaluate the cold start and hot-start real-world NO_x emission levels of Euro-6 passenger cars representing the most common fuel/powertrain/aftertreatment architectures in the market.
- b) To determine the influence of driving and operating conditions parameters of the engine and aftertreatments on the NO_x emissions.
- c) To investigate the effect of high emission peaks on the average NO_x emission levels.
- d) To investigate the real-world operating conditions of a selective catalytic reduction (SCR) system and the relationship with the high instantaneous NO_x emissions.
- e) To determine the impact of high NO_x emission in the accuracy of microscopic prediction of real-world NO_x emissions from SCR-equipped diesel passenger cars.

1.3. Research questions

Based on the stated objectives and with the identified gaps in the literature, the following research questions were answered in this thesis:

Research question 1. What are the real-world NO_x emission levels for the different Euro-6b vehicle technologies?

- **Hypothesis 1.1.** Hot-start NO_x emission levels in RDE tests from Euro-6b vehicle technologies depend on the fuel and aftertreatment technologies.
- **Hypothesis 1.2.** Cold start NO_x emission levels from Euro-6b vehicle technologies depend on the fuel and aftertreatment technologies.

Research question 2. What are the impact and characteristics of the high NO_x emissions from real driving?

- **Hypothesis 2.1.** The high instantaneous NO_x emissions have low occurrence and represent a high amount of total NO_x emissions from real-world tests.
- **Hypothesis 2.2.** The high instantaneous NO_x emissions are related to vehicle, engine and aftertreatment operating conditions.
- **Hypothesis 2.3.** Air-fuel ratio and exhaust gas temperatures, both IOVs, have a strong influence on the NO_x emission from gasoline and diesel vehicles.
- **Hypothesis 2.4.** The efficiency of SCR systems depends on working temperatures, which influences the release of NO_x emission peak.

Research question 3. How does high NO_x emission observations impact the accuracy of microscopic NO_x predictions?

- **Hypothesis 3.1.** A hybrid approach for microscopic NO_x prediction improves the accuracy of its parts: a physics-based model and a machine learning algorithm.
- **Hypothesis 3.2.** NO_x emission peaks influence the total and instantaneous prediction error of microscopic emission models.

1.4. Data used for this thesis

The previous works that provide the data used for the development of this thesis are listed below.

- 1) The following equipment and data were developed at University Institute for the Automobile Research (INSIA), which belongs to the Universidad Politécnica de Madrid (UPM):
 - The portable measurement equipment called MIVECO PEMS, was developed in Prof. Natalia Fonseca's doctoral thesis, and it is described in (Fonseca González et al., 2016; Fonseca González, 2012)

- The RDE test measurement campaign of several Euro 6b sport utility vehicles (SUV) passenger cars was coordinated by Prof. Natalia Fonseca
- 2) The following data and emission model were developed at the Institute of Internal Combustion Engines and Thermodynamics (IVT), which belongs to the Graz University of Technology (TUGraz):
- Several emission tests in the laboratory and in real driving conditions were performed on a Euro 6b diesel passenger car coordinated by Prof. Stefan Hausberger.
 - Data of the vehicle and aftertreatment systems were measured in tests performed in TUGraz to build the vehicle and aftertreatment models for the Passenger car & Heavy-duty Emission Model (PHEM)
 - The development and maintenance of the PHEM for microscopic emission simulation are done by Prof. Stefan Hausberger's research group.

1.5. Structure of the document

CHAPTER 1 – Introduction

This introductory chapter presents the existing problem on NO_x emission from motor vehicles, the objective and research questions to be developed in this thesis, and a brief description of the data used for this study.

CHAPTER 2 – Fundamentals and state of the art

This chapter presents the fundamentals of NO_x emission from motor vehicles and the working principles of NO_x reduction technologies. Then, a review of the state-of-the-art regarding the main topics of this thesis was performed to determine the gaps in the current literature.

CHAPTER 3 - Methodology

This chapter describes the general methodology used for this thesis, followed by the description of the real driving tests used for this work, including the test routes, tested passenger cars, PEMS and measurement equipment, and testing conditions. In addition, common and general calculations are stated for the next chapters, including the methodology to separate the high NO_x emissions peaks.

CHAPTER 4 - Cold start and hot-start NO_x emission levels. Influence of exhaust gas temperature and air-fuel ratio on aftertreatment performance

This chapter focuses on the evaluation of the cold start- and hot-start NO_x emissions of the wide vehicle technologies tested in Madrid. Further, this part demonstrates the relation between the exhaust gas temperature, air-fuel ratio, and performance of NO_x aftertreatments systems installed in different Euro 6b passenger cars. In particular, the

influence of air-fuel ratios on NO_x emission levels from an hybrid electric vehicle (HEV) and a gasoline direct injection (GDI) vehicle is investigated.

CHAPTER 5 - Investigations of the high NO_x emissions from diesel passenger cars

In this chapter, a comprehensive analysis of real-world high instantaneous NO_x emissions in diesel vehicles was carried out using tests performed in Madrid. This chapter examines the impact of high instantaneous NO_x emissions on emission factors and driving time. Further, the analysis identifies the occurrence of NO_x peaks using parameters from the vehicle, engine, and aftertreatment operating conditions.

CHAPTER 6 - SCR efficiency during warm conditions

This chapter presents an in-depth analysis of the SCR behaviour and efficiency in the on-road tests performed in Graz with a Euro 6b diesel passenger car. The analysis also includes the relationship among high NO_x emissions and power, exhaust gas mass and temperatures, and driving modes.

CHAPTER 7 - Influence of high NO_x emissions on microscopic models: Case of a SCR diesel vehicle

The final chapter assesses three microscopic modelling approaches: (a) physics-based (PHEM), (b) data-driven machine learning algorithm (random forest), and (c) hybrid proposed model that uses PHEM predictions as inputs for a random forest model to predict the reduction of engine-out NO_x emissions. The effects of NO_x emission peaks on those microscopic models were studied.

8. Conclusions and future works

This chapter summarises the results from this thesis. The conclusions, main contributions, dissemination of results, and future works are described.

CHAPTER 2

Fundamentals and state of the art

A literature review of the areas addressed in this thesis and possible instruments available for NO_x emission modelling is performed in this chapter. Further, an examination of key concepts as engine-out NO_x emission from ICE and NO_x control technologies for the different ignition types are also presented.

2.1. NO_x emissions regulation

Government agencies approach air pollution control by developing and enforcing air emission standards and air-quality standards. In these standards, permitted emission rates and the standard test procedures are clearly described. Since these tests and analyses were performed using European vehicles, the following descriptions focus on European legislation, and the prevalence of the diesel vehicles in the European market highlights the importance of the description. With successive standards, the important reductions of the regulated pollutants carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NO_x), particulate matter (PM) and the particle number (PN) have been achieved.

The latest standards for type approval emission tests are Euro 6 for light-duty and Euro VI for heavy-duty. **Table 2.1** lists the European emission limits for passenger cars. Type approval NO_x emission limits have been reduced for diesel passenger cars from 500 to 80 mg km⁻¹. This took place between 2000 (Euro 3) and 2015 (Euro 6). In the case of gasoline vehicles, the NO_x emission limits dropped from 150 to 60 mg km⁻¹ for Euro 3 (in 2000) and Euro 5 (in 2011) standards. Those last NO_x emission limits were employed thus far; however, type approval procedures and driving cycles have changed, providing a more robust framework to represent more realistic NO_x emissions with the requirement of more efficient NO_x control technologies. From Euro 1 to Euro 6b, vehicles passed the type approval emission tests only under the NEDC laboratory cycle. However, new car models pass laboratory tests under the world harmonised light vehicles test procedure (WLTP) based on the new cycle WLTC and the real-driving emissions (RDE) tests following a transition period from September 2017.

Table 2.1. European emission standards for passenger cars, M1 category.

Standard	Type Approval	First Registration	CO [g km ⁻¹]	HC [g km ⁻¹]	NO _x [g km ⁻¹]	HC+NO _x [g km ⁻¹]	PM [g km ⁻¹]	PN [# km ⁻¹]
Compression ignition (CI)								
Euro 1 to Euro 4	Jul. 1992 and Jan. 2005	Jan. 1993 and Jan. 2006	2.72 to 0.50	-	NA to 0.25	0.97 to 0.30	0.14 to 0.025	-
Euro 5b*	Sep. 2011	Jan. 2013	0.50	-	0.18	0.23	0.0045	6×10 ¹¹

Euro 6b	Sep. 2014	Sep. 2015	0.50	-	0.08	0.17	0.0045	6×10 ¹¹
Euro 6c	-	Sep. 2018	0.50	-	0.08	0.17	0.0045	6×10 ¹¹
Euro 6d-Temp	Sep. 2017	Sep. 2019	0.50	-	0.08	0.17	0.0045	6×10 ¹¹
Euro 6d	Jan. 2020	Jan. 2021	0.50	-	0.08	0.17	0.0045	6×10 ¹¹
Spark ignition (SI)								
Euro 1 to Euro 4	Jul. 1992 and Jan. 2005	Jan. 1993 and Jan. 2006	2.72 to 1.00	NA to 0.10	NA to 0.08	0.97 to NA	-	-
Euro 5b*	Sep. 2011	Jan. 2013	1.0	0.10	0.06	-	0.0045**	-
Euro 6b	Sep. 2014	Sep. 2015	1.0	0.10	0.06	-	0.0045**	6×10 ¹¹
Euro 6c	-	Sep. 2018	1.0	0.10	0.06	-	0.0045**	6×10 ¹¹
Euro 6d-Temp	Sep. 2017	Sep. 2019	1.0	0.10	0.06	-	0.0045**	6×10 ¹¹
Euro 6d	Jan. 2020	Jan. 2021	1.0	0.10	0.06	-	0.0045**	6×10 ¹¹

*Euro 5a was omitted. From Euro 5a for gasoline, nonmethane hydrocarbons (NMHC) = 0.068 g km⁻¹

** Only for GDI engines.

Adapted from: <https://dieselnet.com>.

The type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) was promulgated in Regulation (EC) No 715/2007. Amendments to this regulation were stated in Commission Regulation (EC) No 692/2008. The RDE test was performed during vehicle operation using a PEMS. The RDE testing requirements were introduced through several regulatory amendments, with the first RDE package Reg. (EU) 2016/427 (March 2016). This consists of test equipment requirements, test trip characteristics, a description of the data evaluation tools, the concept of PEMS vehicle families, and reporting requirements. The second RDE package (April 2016) consists of not-to-exceed (NTE) emission limits and their respective applications; this regulation designation is Reg. (EU) 2016/646. The third package Reg. (EU) 2017/1154 (July 2017) focuses on the inclusion of cold start emissions, PN emissions by gasoline cars, the definition of a test procedure for hybrid technologies, and provisions for the event of an auxiliary emission control devices regeneration. Finally, the fourth package for RDE and concerning WLTP is Reg. (EU) 2018/1832 (November 2018). This package consists of in-service testing and market surveillance. The main document with respect to emission regulation is Reg. (EU) 2017/1151, published in June 2017 and complemented and amended by the aforementioned packages. Each of these packages is prepared and validated by the RDE-LDV, which consists of technical experts; however, it is dominated by stakeholders from the automotive industry. Once a package is finalised, it is proposed to the Technical Committee for Motor Vehicles (TCMV), where national experts from the EU Member States are represented. Finally, it is the European Parliament that is the final authority that can accept or reject the decisions of the TCMV (Hooftman et al., 2018).

For RDE tests, NTE emission values must be accomplished in urban and the total RDE trip; they are computed as

$$NTE_{pollutant} = CF_{pollutant} \cdot Euro\ 6\ emission\ limit \quad (2.1)$$

where $CF_{pollutant}$ corresponds to a conformity factor for a given pollutant. **Table 2.2** lists the conformity factors (CF) and emission limits for the different NO_x Euro 6 standards for passenger cars.

Table 2.2. Euro 6 NTE emission limits for NO_x passenger cars.

Standard	Conformity factor	Deviation [%]	Fuel	NTE [mg km ⁻¹]	Comment
Euro 6b	2.10	110	Diesel	168.0	NEDC cycle. RDE for monitoring only
			Gasoline	126.0	
Euro 6c	2.10	110	Diesel	168.0	WLTC cycle. RDE for monitoring only
			Gasoline	126.0	
Euro 6d-Temp	2.10	110	Diesel	168.0	WLTC cycle + RDE (Temporary CF)
			Gasoline	126.0	
Euro 6d	1.43	43	Diesel	114.4	WLTC cycle + RDE (Final CF)
			Gasoline	85.5	

Valid RDE trips are measured on real roads and traffic conditions and must meet distance, trip composition, and average speed requirements in addition to the dynamic boundary conditions. In general, the boundaries for RDE tests are presented in **Table 2.3**.

Table 2.3. RDE testing boundaries

Trip parameter		Requirements in regulation
Total trip duration		Between 90–120 min
Distance	Urban	>16 km
	Rural	
	Motorway	
Trip composition	Urban	29–44 % of the distance
	Rural	23–43 % of the distance
	Motorway	23–43 % of the distance
Average speeds	Urban	15–40 km h ⁻¹
	Rural	Between 60–90 km h ⁻¹
	Motorway	>90 km h ⁻¹ (>100 km h ⁻¹ for at least 5 min)
Payload		< 90 % of maximum vehicle weight
Altitude	Moderate	0–700m
	Extended	Between 700–1,300 m
	Difference	No more than 100 m altitude difference
	Cumulative gain	1200 m per 100 km
Ambient temperature	Moderate	0°C–30°C
	Extended	–7–0°C and 30–35°C
Stop percentage		Between 6–30 % of urban time

Maximum speed		145 km h ⁻¹ (160 km h ⁻¹ for 3 % of motorway driving time)
Dynamic conditions	Maximum metric	95th percentile of $v \cdot a$ (Speed times positive acceleration)
	Minimum metric	RPA (Relative positive acceleration)
Use of auxiliary systems		Free to use as in real life (operation not recorded)

In addition, in RDE package 3, the cold start is included in the emission calculation within the same average speed than that in the urban phase and with a limit of 60 km h⁻¹. Cold start periods are defined as the first 5 min from first engine start or when the engine coolant reaches 70 °C for the first time. If an emission device regenerates during the first RDE test, then the test is void and it must be repeated. However, if the regeneration occurs in a second test, these events must be included in the results.

2.2. Fundamentals of NO_x emissions from motor vehicles

The internal combustion engines are a source of pollution for the air. The main regulated pollutants in passenger cars include PM, NO_x, HC, volatile organic compounds (VOCs), and CO. This thesis is focused on NO_x emission control and its modelling; therefore, the production of NO_x emissions from ICEs is detailed below. In ICEs, most nitrous emissions are nitrogen oxide (NO), with a small amount of nitrogen dioxide (NO₂), and traces of other nitrogen-oxygen combinations. These are all grouped together as NO_x.

2.2.1. NO_x emissions from motor vehicles

In gasoline and diesel engines, the relative amounts of engine-out NO_x depend on engine design and operating conditions in the order of 500 to 1000 ppm or 20 g kg⁻¹ fuel (Heywood, 1988). The NO_x emissions are not part of the fuel combustion but are produced in the environment created by the combustion reactions.

The combustion process is a fast-exothermic gas-phase reaction. The combustion is stoichiometric when all atoms in the fuel are burned into their corresponding oxides. Air contains nitrogen; however, when the products are at low temperatures, nitrogen is not significantly affected by the reaction, which in principle limits the production of NO_x at these temperatures. Considering an hydrocarbon fuel C_aH_b, the complete combustion equation is

2.2.1.1. Air-fuel ratio

The air-fuel ratio of a combustion mixture determines the combustion chemistry, and consequently the air emissions produced from the combustion process. The stoichiometric air-fuel ratio is

$$(A/F)_s = \frac{M_{fuel}}{\left(a + \frac{b}{4}\right) \cdot M_{air}} \quad (2.3)$$

where M_{fuel} is the molecular mass of the fuel, and M_{air} is the molecular mass of air. The air-fuel ratio depends on fuel composition, and in real-world conditions, the stoichiometric combustion is not always feasible. An important parameter to know the fuel supply and the “correct” combustion mix is the relative air-fuel ratio, which is defined as

$$\lambda = \frac{(A/F)_{actual}}{(A/F)_s} \quad (2.4)$$

where the actual air-fuel ratio is divided for the stoichiometric air-fuel ratio. Another form for the same characteristic parameter is the fuel-air equivalence ratio (ϕ), defined as the inverse of the relative air-fuel ratio

$$\phi = \frac{1}{\lambda} = \frac{(F/A)_{actual}}{(F/A)_s} \quad (2.5)$$

Therefore, a lean mixture is characterised by ($\phi < 1$, $\lambda > 1$), while a rich mixture is characterised by ($\phi > 1$, $\lambda < 1$).

The fuel used in spark-ignition (SI) engines is more volatile than diesel, and the air-fuel mixing process prior to combustion also extends over a longer period than that in a diesel engine. The result is that SI engines operate on a more homogenous mixture than their diesel counterparts. On one hand, SI engines run on a mixture in the stoichiometric range ($\phi = 1$). On the other hand, diesel engines, on the other hand, always operate with excess air ($\phi < 1$). An air deficiency ($\phi > 1$) results in increased soot, CO, and HC emissions (Bosch, 2002)

2.2.1.2. NO_x formation mechanism

The main source of NO is the oxidation of atmospheric nitrogen. NO is formed through three primary mechanisms (Rapp et al., 2016), as listed below

- Thermal mechanisms, i.e., Zeldovich mechanism
- Nonthermal mechanisms, e.g., Fenimore or nitrous oxide
- Fuel nitrogen mechanisms, in which nitrogen in the fuel is converted to NO.

Thermal NO

For the analysis above, using simple chemical stoichiometry in Equation (2.2), it was assumed that nitrogen (N_2) is inert and does not react with oxygen. This is no longer true when the reaction temperature is sufficiently high. Thus, NO is produced by the oxidation of N_2 in the air through the following chemical reaction (Tan, 2014)

$$K_{P,\text{NO}} = 4.71 \exp\left(-\frac{10900}{T}\right) \quad (2.7)$$

As indicated by the formula for the equilibrium constant ($K_{P,\text{NO}}$), the oxidation of nitrogen proceeds slowly at low temperatures; however, extremely fast at high temperatures. The formation of NO from molecular nitrogen was first proposed by (Zeldovich et al., 1947). NO formed by this mechanism is called Zeldovich mechanism or thermal NO, where near-stoichiometric fuel-air mixtures cause the formation and destruction of NO, and are described by

Thermal NO formation was first introduced in the 1940s. Thermal NO formation is very sensitive to combustion temperature, and its formation is negligible when the temperature is 1000 °C or lower. The rate of NO formation is significant and increases exponentially when the temperature is over 1400 °C. The reactions in **Table 2.4** are used to describe the step reactions of thermal NO formation.

First, the concentration of oxygen atoms required to initiate the reaction is strongly dependent on temperature because more oxygen atoms are available to the reaction at a higher temperature. Second, this reaction produces nitrogen atoms, which is the bottleneck that limits the rate of NO formation, which is also sensitive to temperature.

Table 2.4. Rate constants for Thermal NO formation

Reaction	Rate constant [cm ³ mol ⁻¹ s ⁻¹]	Temperature range [K]
$\text{N}_2 + \text{O} \xrightarrow{k_1^+} \text{NO} + \text{N}$	$k_1^+ = 7.6 \times 10^{13} \exp\left(-\frac{38000}{T}\right)$	2000–5000
$\text{N}_2 + \text{O} \xleftarrow{k_1^-} \text{NO} + \text{N}$	$k_1^- = 1.6 \times 10^{13}$	300–5000
$\text{N} + \text{O}_2 \xrightarrow{k_2^+} \text{NO} + \text{O}$	$k_2^+ = 6.4 \times 10^9 T \cdot \exp\left(-\frac{3150}{T}\right)$	300–3000
$\text{N} + \text{O}_2 \xleftarrow{k_2^-} \text{NO} + \text{O}$	$k_2^- = 1.5 \times 10^9 T \cdot \exp\left(-\frac{19500}{T}\right)$	1000–3000
$\text{N} + \text{OH} \xrightarrow{k_3^+} \text{NO} + \text{H}$	$k_3^+ = 4.1 \times 10^{13}$	300–2500
$\text{N} + \text{OH} \xleftarrow{k_3^-} \text{NO} + \text{H}$	$k_3^- = 2.0 \times 10^{14} \exp\left(-\frac{23650}{T}\right)$	2200–4500

Adapted from (Heywood, 1988)

where k_i^+ and k_i^- are the forward and reverse rate constants, respectively. The net rate of NO formation under constant pressure and the temperature condition can be calculated by considering all step reactions listed in **Table 2.4**

$$\frac{d[\text{NO}]}{dt} = \{k_1^+[\text{N}_2][\text{O}] - k_1^-[\text{NO}][\text{N}]\} + \{k_2^+[\text{N}][\text{O}_2] - k_2^-[\text{NO}][\text{O}]\} + \{k_3^+[\text{N}][\text{OH}] - k_3^-[\text{NO}][\text{H}]\} \quad (2.11)$$

where $[]$ denote species concentrations (mol cm^{-3}). Note that most forward and reverse rate reactions have large activation energies that result in the strong temperature dependence of NO formation rates (Heywood, 1988). Introducing equilibrium assumptions and the initial values of $d[\text{NO}]/dt$, the initial NO formation rate can be written as:

$$\frac{d[\text{NO}]}{dt} = \frac{6 \times 10^{16}}{T^{1/2}} \exp\left(-\frac{69090}{T}\right) [\text{O}_2]_e^{1/2} [\text{N}_2]_e \quad (2.12)$$

The strong dependence of $d[\text{NO}]/dt$ on the temperature in the exponential term is evident. **Figure 2.1** shows the NO formation rate as a function of gas temperature and fuel-air ratio equivalence ratio in postflame gases, and also shows the adiabatic flame temperature. For adiabatic constant-pressure combustion (an appropriate model for each element of the fuel that burns in an engine), this initial NO formation rate peaks at the stoichiometric composition and decreases as the mixture becomes leaner or richer.

NO forms in both, the flame front and the postflame gases. However, in engines, the combustion occurs at a high pressure, and therefore, the flame reaction zone is extremely thin (~ 0.1 mm) and the residence time within this zone is short. Further, the cylinder pressure rises when most of the combustion process attaining higher temperature than they reached immediately after combustion. Thus, NO formation in postflame gasses almost always dominates any flame-front-produced NO.

Figure 2.1. Initial NO formation rate (mass fraction per second) as a function of temperature for different equivalence ratios at 15 atm pressure. The dashed line shows the adiabatic flame temperature for kerosene combustion with 700 K, 15 atm air. Source (Heywood, 1988)

Prompt NO

(Fenimore, 1971) found that some NO formed during combustion could not be explained by the Zeldovich mechanisms. When the equivalence ratio is greater than 1, the nitrogen in the air reacts to form hydrogen cyanide (HCN) through the following chemical reaction (Tan, 2014)

Since there are oxygen-containing compounds in the combustion system, the HCN produced in the above reaction, and the nitrogen atom reacts further to produce NO through several chain reactions.

Prompt NO is formed only in a combustion zone of the flame where the combustion is incomplete, and the hydrocarbon radicals are present. These reactions occur rapidly; thus, it is called prompt NO. The formation of prompt NO does not significantly depend on temperature in comparison with thermal NO. Further, prompt NO is formed mainly under lower temperature conditions during a short residence time. Other types of chain reactions can lead to non-thermal mechanisms for NO production.

Fuel nitrogen mechanisms

The amount of nitrogen in fuel varies depending on the type of fuel and the refining process used. Although diesel fuels contain more nitrogen than gasoline, the NO production levels are not significant. Fuel NO is sensitive to stoichiometry instead of temperature because it forms readily at considerably low temperatures.

Formation of NO₂

According to (Heywood, 1988), chemical equilibrium considerations indicate that for burned gases at typical flame temperatures, NO₂/NO ratios should be negligibly small. While experimental data show that this is true for SI engines, in CI engines, the ratio of NO₂/NO_x can be up to 0.1–0.3. A plausible mechanism for the persistence of NO₂ is that NO formed in the flame zone can be converted rapidly to NO₂ via reactions such as

Subsequently, the conversion of this NO₂ to NO occurs via

Unless the NO_2 formed in the flame is quenched by mixing with a cooler fluid, this explanation is consistent with the higher NO_2/NO ratio occurring at a high load in CI engines, because of the widespread presence of cooler regions which could quench the conversion back to NO.

2.2.1.3. Spark-ignition (SI) engines

A flame is a combustion reaction that can propagate sub-sonically through space. The reaction zone is usually called the flame front. This flame characteristic of spatial propagation results from the strong coupling among the chemical reaction, transport processes of mass diffusion and heat conduction, and fluid flow. The conventional spark-ignition flame is thus a premixed (fuel and oxidiser are essentially uniformly mixed together) unsteady turbulent flame, and the fuel-air mixture through which the flame propagates is in the gaseous state (Heywood, 1988)

The most important engine variables that affect NO emissions are fuel-air equivalence ratio, burned gas fraction of the in-cylinder unburned mixture, and spark timing.

Equivalence ratio

The NO_x curve as a function of air-fuel ratios takes the bell shape as shown in **Figure 2.2**. NO_x production in conventional SI engines depends highly on combustion temperature. The higher the temperature, the greater is the tendency to oxidise nitrogen compounds into NO_x . Maximum burned gas temperatures occur at $\phi \approx 1.1$; however, under these conditions, the oxygen concentrations are low. The maximum value of NO_x for a given engine load and speed invariably occurs at an equivalence ratio less than 1.0 ($\phi \approx 0.9$) although the temperature is lower than that for a richer mixture, and the available oxygen concentration is considerably higher.

Figure 2.2. Variation of pollutants concentration (HC, CO, and NO) in the exhaust of a conventional SI engine with fuel-air equivalence ratio. Source (Heywood, 1988)

The most widespread SI engines in use are homogenous-charge spark-ignition (HCSI) engines. In general, the fuel is injected just upstream of the intake port with a low-pressure injector; these engines are called port fuel injection (PFI) engines. Because the fuel and air mix during both the intake and compression strokes, they are assumed to be homogenous.

Ignition timing

NO_x can be correlated with ignition timing. If an ignition spark is advanced, the combustion occurs earlier in the cycle, which increases the peak cylinder pressure because more fuel is burned before the top centre (TC) crack position and the peak pressure moves closer to TC where the cylinder volume is smaller. Therefore, the cylinder temperature will be increased, and more NO_x will be created; further, HC and fuel consumption increase. **Figure 2.3** shows the correlation between the NO concentration and ignition time advance.

Figure 2.3. Correlation between NO concentration and ignition time advance. At 1600 rpm, $n_v = 50\%$. Left-hand of the curve corresponds to the maximum brake-torque (MBT) timing for each A/F curve. BTC = before top centre. Source (Heywood, 1988)

Burned gas fraction

The unburned mixture in the cylinder contains fuel, vapour, air, and burned gases (Heywood, 1988). The burned gases are residual gas from the previous cycle and any exhaust gas recycled to the intake for NO_x emission control. The residual gas fraction is influenced by load, valve timing (particularly the extent valve overlap), and, to a lesser degree, by speed, and air-fuel ratio. The burned gases act as a diluent (increasing heat capacity) in the unburned mixture; the absolute temperature reached after combustion varies inversely with the burned gas mass fraction. Hence increasing the burned gas fraction reduces the NO emissions levels. The primary effect of the burned gas diluent in the unburned mixture on the NO formation process is that it reduces flame temperatures. **Figure 2.4** shows the effect of increasing the burned gas fraction by recycling exhaust gases into the intake system.

Figure 2.4. Variation of exhaust NO concentration with the percentage of recycled exhaust gas (by EGR). SI engine, 1600 rpm, $n_v = 50\%$, MBT timing. Source (Heywood, 1988)

Lean operation in SI engines

The benefit of operating at lean concentrations, in addition to achieving higher efficiency, is that at values of ϕ less than about 0.9, the CO production is negligible, HC emissions are near the minimum level, and NO emissions are greatly reduced (**Figure 2.2**). As ϕ decreases even further (less than 0.7), there is a trade-off between the further reduction in NO_x emissions and an increase in HC emissions and CO emissions because of incomplete combustion or quenching. Therefore, a lean operation can be an excellent control strategy for reducing emissions (Rapp et al., 2016). The GDI engines are replacing conventional PFI-SI engines with increasing frequency. In GDI engines, the fuel is directly injected into the engine cylinder, and it depends on injection timing; they can produce a highly stratified charge.

Thus, the close-loop control for $\phi < 1$ (lean-burn control) has the main advantage of the reduction of fuel consumption caused by a lean-burn (non-throttled) operation. The success of this concept depends to a high degree on the availability of catalytic converters that can reduce NO_x emissions during the lean-burn operation. The lean-misfire limit (LML) for SI engines in the lean-burn range reaches $\phi \approx 0.6$ regardless of engine design measures (Bosch, 2002).

2.2.1.4. Compression-ignition (CI) engines

In the diesel engine, the fuel is injected into the cylinder into the air already at high pressure and temperature, near the end of the compression stroke. The autoignition, or self-ignition, of portions of the developing mixture of already injected and vaporized fuel with this hot air, starts the combustion process rapidly. Burning then proceeds as a fuel and air mix to the appropriate composition for combustion. Thus, fuel-air mixing plays a controlling role in the diesel combustion process (Heywood, 1988).

Non-uniform burned gas temperature and composition result from this nonuniform fuel distribution during combustion. The air-fuel mixing and combustion processes are extremely complex. The diesel engine combustion process is predominantly an unsteady turbulent diffusion flame, and the fuel is initially in the liquid phase. If the reactants are

not premixed and must be mixed in the same region where the reaction takes place, the flame is called a diffusion flame because the mixing must be accomplished by a diffusion process.

The most important engine variables that affect NO emissions are the injection timing, air-fuel ratios, and burned gas fraction.

Injection timing

The start of injection, rate-of-discharge curve, and atomisation of the fuel affect pollutant emissions. The point at which combustion starts is a function of the start of injection (injection timing). Delayed injection reduces NO_x emissions, whereas excessive delay results in increased fuel consumption and HC emissions. A deviation of the start of injection in 1° (crankshaft) from the setpoint can increase NO_x emissions or HC emissions by as much as 15 % (Heywood, 1988).

Figure 2.5 shows how the ratio of the average cylinder NO concentration divided by the exhaust concentration varies during the combustion process. NO concentrations reach the maximum shortly after the curve reaches the peak pressure; there is a modest amount of NO decomposition. Variations in engine speed have little effect on the shape of this curve.

Figure 2.5. Ratio of cylinder-average NO concentration at given crank angle to exhaust NO concentration. Diesel engine, $\phi = 0.6$, injection timing at 27 °C BTC. Source (Heywood, 1988)

The critical period is when burned gas temperatures are at the maximum, i.e., between the start of combustion and shortly after the occurrence of the peak cylinder pressure. After peak pressure, burned gas temperatures decrease as the cylinder gases expand. The 20° crank angle after the start of combustion is the critical period, and almost all of the NO forms within 20° following the start of combustion. If the injection timing is retarded, the combustion process is retarded, the NO formation occurs later, and the concentrations are lower because the peak temperatures are lower.

Equivalence ratio

An increase in the fuel-air equivalence ratio results in an increase in the maximum average gas temperature, and in an increase in NO_x concentration in the exhaust. The effect of the overall equivalence ratio on NO concentrations is shown in **Figure 2.6**. The NO levels increase at high loads with higher peak pressures, where the temperatures are

higher, and the regions of close-to-stoichiometric burned gas are higher. Both NO and NO_x concentrations were measured; NO₂ is 10–20 % of the total NO_x in CI engines. Though NO levels decrease with a decreasing overall equivalence ratio, they do so much less rapidly than that for SI engine NO emissions owing to the nonuniform fuel distribution in diesel (Heywood, 1988).

Figure 2.6. Exhaust NO_x and NO concentrations as a function of overall equivalence ratio or engine load. Diesel engine, 1000 rpm, injection timing at 27 °C BTC. Source (Heywood, 1988)

Burned gas fraction

Since the thermal NO_x production is the same for SI and CI engines, the increase in the burned gas fraction reduces the amount of oxygen in the fresh intake charge while increasing its specific heat. This reduces the peak flame temperatures and NO_x emission production. This parameter is controlled using EGR systems in the diesel engines of modern vehicles.

Intake-air temperature

The combustion temperature increases along with an increase in the temperature of the intake air, and this leads to an increase in NO_x emissions. Charge-air cooling (intercooling) is an effective strategy to minimise NO_x formation in turbocharged engines

2.2.2. NO_x emission control technologies

NO_x control technologies can be classified by point of control as pre-combustion, in-combustion, and post-combustion methods. Pre-combustion methods are the most cost-effective because elements that may be converted into air pollutants in a combustion process are removed from the fuels. Examples include coal washing, crude oil refinery, and natural gas sweetening (Tan, 2014). However, NO production levels from fuel components are not significant for diesel and gasoline engines. In-combustion methods include combustion process modifications, and strategies closely related to the above-mentioned variables to control NO_x formation.

Post-combustion methods (aftertreatment systems) are usually required to minimise engine-out NO_x emission levels to satisfy air emission standards. The only satisfactory method known for the removal of NO from exhaust gas involves catalytic processes. Different technologies have been developed for automotive applications and each differs according to fuel use and the type approval limit regulations.

The main technologies to reduce NO_x emissions in modern diesel vehicles are exhaust gas recirculation (EGR), complemented with aftertreatment technologies such as LNT and/or SCR systems. In gasoline engines, TWCs are widely implemented. The commercial application of EGR systems in light-duty vehicles began in 1992 on Euro 1 vehicles (Jääskeläinen and Khair, 2019). This system has been in common use in modern diesel vehicles, which reflects the positive effects of EGR systems on NO_x reduction as demonstrated for SI and CI engines. In terms of aftertreatments, TWCs, introduced in the 1980s, best reduce NO_x at stoichiometric air-fuel ratios and under rich (excess fuel) conditions; however, they cannot control NO_x under lean (excess air) conditions. This makes TWCs unsuitable for diesel applications. An evolution of TWC is the LNT; alkaline metals are included to adsorb NO_x under lean conditions, typically lasting 60–120 s. Adsorbed NO_x is later converted to N_2 by operating under rich conditions for a few seconds, typically 1–5 s (DiGiulio et al., 2014; Lambert, 2019). This technology was first implemented in GDI engines and then commonly used in diesel engines around 2009 for Euro 5 vehicles. However, LNT systems have a limited NO_x reduction efficiency compared to SCR catalysts because their rich air-fuel operation during the de- NO_x process causes unstable engine operation and increases fuel penalty (Myung et al., 2017). More stringent NO_x limits for diesel vehicles led to the broad implementation of SCR systems in Euro 6 diesel passenger cars from 2015. However, the change in the type approval testing procedure in 2017 to a more realistic WLTC cycle and RDE tests have enforced SCR systems to higher efficiencies in real-world conditions.

Figure 2.7. Conversion efficiency for NO_x , CO, and HC of a TWC. Source (Depcik and Assanis, 2005)

For homogeneous-charged SI engines, the aftertreatment device is TWC because it is extremely effective at simultaneously oxidising HC and CO, and for reducing NO_x , provided the engine operates at a stoichiometric fuel-air mixture (**Figure 2.7**). The conversions of NO, CO, and hydrocarbons in a TWC operated with cyclical variations in the equivalence ratio are larger than the estimates based on the summation of steady-state values during the cycle. Because of these cyclic variations in the exhaust gas composition about a set point close to stoichiometric, it is desirable that the catalyst be able to reduce NO when a slight excess of oxygen is present (on the lean side) and remove CO and HC when there is a slight deficiency of oxygen (on the rich side). The close-loop control for $\phi = 1$ is required to operate the engine within a very narrow range in which

$\phi = 1 \pm 0.005$ (catalytic-converter window). Such precision can only be achieved with precise closed-loop control of the air-fuel mixture with a lambda oxygen sensor installed upstream of the converter. A second lambda sensor installed downstream of the catalytic converter increases the precision further (Bosch, 2002).

Urea catalytic selective converters can reduce NO_x emissions from diesel and lean-burn engines to meet stringent environmental regulations (Nova and Tronconi, 2014); however, this aftertreatments need to maintain a thermal window for the best de NO_x efficiency. Several parameters affect their performance including exhaust gas flow conditions such as velocity and mass flow rates; substrate and coating materials; type of mixers and injection characteristics; and among others. Furthermore, the efficiency of the most popular SCR catalysts such as vanadium-based, Cu-zeolite and Fe-zeolite catalysts can be strongly affected under 200 °C. These operating temperatures are recurrent conditions of urban and low load. Urea should be injected at $T > 180$ °C to avoid the formation of ammonium nitrate (NH_4NO_3), which causes activity inhibition, solid deposits and progressive damage of catalyst (Ruggeri et al., 2018). Under cold start, which is typical of urban driving, light-off temperatures are difficult to reach because of the thermal inertia and heating of exhaust elements (Chan and Hoang, 1999; Roberts et al., 2014).

2.3. State of the art

2.3.1. NO_x emissions under real-world driving

In the existing literature, there is an increasing number of studies that analyse NO_x emissions of passenger cars with PEMS, even in tests that are compliant in a greater or lesser extent with the requirements of the RDE regulation. However, the events of the highest instantaneous NO_x emissions, their impact on real-world emissions, and their relationship with the operating parameters of the vehicle, engine and aftertreatment systems are barely analysed.

On the one hand, stringent emission limits have reduced the NO_x emission levels from modern diesel vehicles, by the application of SCR systems (Carslaw et al., 2019; Hooftman et al., 2018). On the other hand, real-world emissions surpass emission limits and show variability between the existing fleet. Some studies compared large number of vehicles to understand the emission levels of the vehicle fleet. In general, those studies are part of reports, commonly carried out by the Joint Research Centre (JRC). According to the last report of JRC, post-Euro 6b diesel vehicles show lower emissions than diesel Euro 6b fleet. However, there is wide vehicle-to-vehicle variability in every Euro 6 stage and particular cases of high emitters are also found (Valverde et al., 2020, 2019a). In an extensive study, (O'Driscoll et al., 2018), compared the real-world NO_x emissions of 149 Euro 5 and 6 diesel, gasoline and hybrid vehicles to demonstrate the difference between type-approval and real-world CO_2 and NO_x emissions. Evidence from remote sensing (RS) shows that post-diesel gate has reduced the NO_x emission levels by fixes on software

and hardware (Grange et al., 2020). However, further regulations and investigations are still required.

For Euro 6 diesel passenger cars in real-world conditions, (Luján et al., 2018) used a vehicle with LNT in an RDE route to compare the moving averaging window (MAW) and power binning (PB) methods to compute NO_x emissions. Further, they analysed cold start emissions. (Gallus et al., 2017) analysed the influence of driving style and road grade in one EGR-only vehicle. (Triantafyllopoulos et al., 2019) analysed the RDE testing and boundary conditions, and they found that outside the boundaries set in the RDE regulation emissions tend to exceed the limits. (Triantafyllopoulos et al., 2018) confirmed the potential to reduce NO_x emissions by reconfiguring EGR behaviour and implementing an SCR system. One gasoline and two diesel Euro 6b vehicles were assessed by (Yang et al., 2020), the study found higher pollutants in motorway for gasoline vehicles and in urban for the diesel vehicles. Particularly, for high-speed driving conditions, the gasoline vehicle was more affected than the diesel vehicles. The emission rates of 122 US light-duty vehicles were compared between real-world routes and certification levels by (Khan and Frey, 2018). Another identified gap was the lack of analysis on the effect of air-fuel ratios on emission and NO_x reduction of TWC-equipped gasoline vehicles.

Outside Europe, several vehicles with LNT were tested by (Kwon et al., 2017) to analyse: different driving routes, the impact of ambient temperatures, and the use of air conditioner as well as to compare MAW and PB calculating methods. In Korea, 17 SCR and LNT vehicles were tested in two different RDE routes by (Cha et al., 2019), the average NO_x emissions of most test vehicles approximately exceeded 6.6 times the emission limit on test routes. The LNT vehicles presented approximately two times the NO_x emission levels of SCR vehicles. (Chong et al., 2018) analysed four LNT diesel vehicles in an attempt to relate vehicle specific power (VSP) values to emissions and fuel consumption. (H. Wang et al., 2018) analysed the effect of altitude up to ~3000 m in four cities in China.

2.3.2. Cold start and influence of exhaust gas temperatures on NO_x emissions

Low operating temperatures of aftertreatments are present during cold start and appear at low loads during warm-engine driving. In the literature, there is a lack of real-world comparison of different Euro 6 powertrains/aftertreatments instantaneous NO_x emissions during cold start. Cold start primarily occurs in urban areas (Weiss et al., 2017), and particularly in most local and populated streets (Faria et al., 2018) which are important for urban air quality. During cold start, the catalysts need to attain the light-off conditions, which is the point at which the catalyst acquires a sufficiently high temperature to enable chemical reactions (Bannister and Taylor, 2014). In addition, urban low-load driving conditions limit exhaust gas temperatures, thereby decreasing the thermal heat transfer from combustion to the aftertreatment systems (Chan and Hoang, 1999; Roberts et al., 2014). In contrast, during warm-engine driving,

aftertreatment devices can be affected by cooling conditions during zero or low engine load and long motoring, i.e. stopping, braking, and deceleration.

In the literature, the cold start and to a lesser extent the cooling down of exhaust aftertreatment systems have been studied from the aftertreatment device and from the vehicle and testing boundary conditions standpoint. First, there are several articles on catalyst modelling, simulation, and analysis (Chan and Hoang, 1999; Colombo et al., 2014; Koltsakis et al., 2011; Ramanathan et al., 2004; Schmeisser et al., 2013; Tronconi et al., 2005). Second, from the perspectives of the entire vehicle, CO₂ and pollutants from the cold start were modelled by (Weilenmann et al., 2013). In addition, Euro 6 vehicles were studied in regulated driving cycles and real-world driving conditions (Dardiotis et al., 2013; Faria et al., 2018; Luján et al., 2018; Myung et al., 2017; Suarez-Bertoa et al., 2019; Valverde et al., 2019b; Weber et al., 2019). Finally, the boundary conditions that affect the cold start of Euro 6 vehicles were related to ambient temperature (Chong et al., 2018; Grange et al., 2019; Suarez-Bertoa and Astorga, 2018), parking time, and other variables (Favez et al., 2009; Weiss et al., 2017).

2.3.3. Performance of SCR systems in real driving conditions

A detailed analysis on the SCR deNO_x performance under real-driving conditions focusing on the highest instantaneous emissions and SCR's operating conditions is lacking. The SCR performance has been analysed in a laboratory or via engine tests in several studies. Most of these investigations focus on the analysis of tailpipe NO_x emissions for the fulfilment of regulations and to determine their relationship with several parameters. Using SCR core monolith samples and SCR devices, some studies have investigated the phenomenology, behaviour and modelling of SCR systems (Ciardelli et al., 2004; Colombo et al., 2014, 2012; Konstantinidis et al., 1997; Please et al., 1994; Tronconi et al., 2005; Tronconi and Forzatti, 1992; Tsinoglou and Koltsakis, 2007). Using a diesel engine, an analysis was carried out of the influence of exhaust gas temperatures and flow rate on ammonia storage and slip in transient conditions (Zhao et al., 2011). Other studies analysed the general performance of SCR-equipped vehicles using tailpipe emission factors or by comparing those emissions with driving parameters. According to (Kadijk et al., 2015), the main parameters that determine the conversion rate of SCR systems are

- The size of the SCR catalyst and the exhaust mass flow rate.
- The operating temperature of the exhaust gas and the SCR catalyst.
- The exhaust gas composition, more specifically the available share of NO₂.
- The NO_x mass flow rate which is offered to the SCR catalyst.
- The amount of added AdBlue (NH₃/NO_x – ratio).
- The homogeneity of the NO_x/NH₃ gas mixture.
- The AdBlue storage capacity of the SCR catalyst.

Recently, stress has been considered to improve low-temperature deNO_x performance for a cold start and urban driving conditions (Guan et al., 2014). While the engine

operational approach does not need additional elements, it becomes less efficient in terms of fuel penalty because of indirect use of heating power (Gao et al., 2019b). In fact, between 15–40 % of fuel energy is usually wasted in exhaust gases (Hsiao et al., 2010; Roberts et al., 2014; Yu et al., 2015). Simpler strategies to locate the catalyst close to the engine increase the amount of heat transferred to the SCR, but it may cause thermal sintering, thermal ageing which reduce its lifetime and high temperatures compromise the efficiency (Gao et al., 2019b; Praveena and Martin, 2017). On the other hand, the heating of the catalyst systems improves the deNO_x efficiency and reduces the light-off time. However, the addition of heating elements increase the complexity and cost of the system with the disadvantage of fuel penalty and consequently the increase of CO₂ emissions. Nonetheless, it provides more flexibility for the thermal management of the aftertreatment system (Gao et al., 2019b). The balance between pollution and GHG reduction becomes an important parameter to consider. Regarding SCR heating, some studies analyse or simulate the heating, but there is no estimation of deNO_x improvement coupled to the CO₂ penalty for real driving conditions. There is a deficiency of advanced control strategies for catalyst heaters and an appropriate indicator that can evaluate optimal heating to reduce CO₂ penalty with the maximum NO_x reduction (Gao et al., 2019b).

2.3.4. NO_x modelling

Simulation models are a practical solution to predict vehicle emissions. However, some of the numerical tools referred are too complex to account for the exact vehicle characteristics and driving profile; however, others are too simple and too generic to provide an accurate analysis (Duarte et al., 2015). Therefore, several modelling objectives, approaches and methodologies have been developed for some time. A classification of vehicle model characteristics is shown in **Figure 2.8**, based on the reviews in the literature (Boulter et al., 2006a; Franco et al., 2013; Park et al., 2016).

Figure 2.8. Classification of emission model characteristics. The green boxes correspond to the elements investigated in this thesis.

In general, according to the level or scope of the emission model, different methods can be classified between macroscopic, mesoscopic and microscopic levels. The macroscopic models estimate fleet emissions over a region or at country scale. Macro models use the average speed, vehicle kilometre activity, and fleet characteristics as inputs. The advantage is that macro models do not require detailed input data such as instantaneous vehicle activity (Franco et al., 2013). Mesoscopic models attempt to model street or regional areas, usually using traffic data. One approach is to use the traffic situation models that incorporate both average speed and driving dynamics into emission calculations. In these models, each traffic situation is defined qualitatively based on the road type and the traffic condition (e.g. stop-and-go, urban congested, urban free flow, etc.) (Samaras et al., 2019). One well-established model is the Handbook Emission Factors for Road Transport, HBEFA (Keller et al., 2017), which is supported by a microscopic model, PHEM (Hausberger, 2003) – Passenger Car and Heavy Duty Emission Model.

Microscopic emission models predict instantaneous emissions in short time steps, often in one second, and are useful to predict emissions using driving profiles on single roads. Power is commonly the main explanatory variable, and this and other input variables

can be synchronised or not. To apply instantaneous models, detailed and precise measurements of vehicle operation and location are required; otherwise, any potential benefits may be lost. This is likely to be rather difficult for many model users, as such information is relatively expensive to collect. As a consequence, the use of instantaneous models has been restricted to the research community (Boulter et al., 2006b). Most models are focused on hot-start emissions, and cold-start emissions usually are corrected by correction factors. Cold start becomes difficult to model because the powertrain and aftertreatments are not in normal operation conditions, and their behaviours constantly change during this period (Roberts et al., 2014). The following table lists the most common models for the modelling scope (spatial resolution).

Table 2.5. Examples of emission models and their typical spatial resolution.

Scale	Emission model
Micro	PHEM, CMEM, CRUISE, P4P, MOVES
Meso	HBEFA, COPERT
Macro	EMFAC, ARTEMIS, COPERT

Source (Samaras et al., 2019)

Regarding the input data for the models, in the past, roller bench was common for light-duty vehicles and passenger cars, while engine bench was preferred for heavy-duty vehicles for logistics and power management of the roller bench. In these cases, test operators have control over the test cycle being followed, the environmental conditions and other parameters, and thus, they contribute to the repeatability of results (Franco et al., 2013). Currently, the development of PEMS, remote sensing (RS) and other new techniques have led to test in real-world conditions several types of emissions, increasing the amount of data, the amplitude of testing conditions, and the measured variables. The development of optical remote sensing techniques for measuring traffic emissions began in the 1980s (Bishop et al., 1989). On-road RS provides a large number of measurements under real-driving conditions and produces an accurate result for averaged fleet emission. However, RS has limitations that exclude emissions from idle or deceleration, only measures hot emissions, measures main pollutants but not particle number, etc. A practical application of RS is the fleet emission monitoring and detection of high emitters (Pujadas et al., 2017), and studies combined air quality measurements (Smit et al., 2019). Several studies with RS reported high NO_x levels, concluding the no compliance of last regulations in real-world driving conditions (Carslaw et al., 2013a; Chen and Borken-Kleefeld, 2014).

This study focuses on microscopic level emission modelling of hot-start conditions using data from onboard measurements (PEMS); the accuracy of this measurement equipment have been improved continuously as compared to laboratory-grade systems. The PEMS records instantaneous emission rates and other useful internally observable variables (IOVs) and externally observable variables (EOVs); therefore, PEMS are composed of gas analysers with different measurement technologies, exhaust flow meters, GPS and weather stations, and on-board diagnosis (OBD) port recording data. The PEMS is now widely used, and the rich amount of recorded data becomes useful for emission modelling. PEMSs are used for multiple tasks, such as for testing new type-approval

legislation, identifying gaps in emission knowledge, investigating of aftertreatment systems, and creation of emission maps (Matzer et al., 2017); currently, PEMS has become useful for the validation of emission models.

For the modelling of microscale emissions, analytical and physical approaches were divided into different components that correspond to physical phenomena associated with vehicle operation and emissions production. Each component of the process is then modelled as an analytical representation consisting of various parameters that can characterise the process. Examples of physically based models are Cruise and PHEM, where the speed profile is the input to predict emissions from a vehicle and systems models. Other approach consists of the binning of data (generally power, speed, and acceleration as explanatory variables), e.g., VSP in MOVES.

Frey et al. compared different data-driven approaches and evaluated the explanatory power of IOV and EOVS variables to predict fuel and emissions (Frey et al., 2010). The compared approaches were VSP binning, linear and polynomial regression, time series with moving average and time series regression, and physics-based models. The results indicated that IOVs have higher explanatory power. However, IOVs are more difficult to obtain than EOVSs. (Fernandes et al., 2019) demonstrated the need for parameters from the thermal management of aftertreatments for better predicting NO_x emissions if IOVs or EOVSs are used for modelling. A well-known data-driven model is VERSIT+ (Smit et al., 2007), which was developed by Netherlands Organisation for Applied Scientific Research (TNO), and is based on generalised linear models (GLM) to estimate emissions at local, regional and national levels. The Virginia Tech microscopic model (VT-micro) (Rakha et al., 2004) and the Comprehensive Modal Emissions Model (CMEM) (An et al., 1997; Barth et al., 2000) include operation modes. While VT-micro is a log-polynomial model with speed and acceleration as inputs, CMEM uses VSP and a function of catalyst reduction of emissions. Models based on more complex methodologies are, for example, a model to relate tailpipe emissions and vehicle activity based on a generalised additive model for location, scale, and shape (GAMLSS), and they use VSP and its components as explanatory variables (Hajmohammadi et al., 2019).

There are few advanced machine learning models applied to the prediction of NO_x emissions. The use of advanced machine learning techniques may be useful in estimating vehicular emissions when the problem is highly complex, non-linear and cannot be handled by traditional methods. The reported machine learning-based models that predict real-world NO_x emissions at the micro scale level are scarce. Jaikumar et al. developed an artificial neural network (NN) based model with nonlinear autoregressive exogenous inputs (NARX). The model uses as predictors engine and vehicles speeds, acceleration and VSP, and predicts pollutants for Euro 4 diesel passenger cars (Jaikumar et al., 2017). According to Qi et al., vehicle emissions in a given time can be affected by not only the current driving state but also the past driving state (Qi et al., 2004). For buses, (Pan et al., 2019) applied gradient boosted regression tree (GBRT) to predict emissions from different bus fuel types using past events as inputs for the model. The model uses as inputs the current VSP and acceleration and speed values from the past 10

s. This model showed results that outperformed predictions of the VT-Micro model. (C. Wang et al., 2018) used back propagation neural networks (BPNN) to predict emissions based on three predictors: the current VSP and one past second speed and acceleration. The models performed better than the different combinations of polynomial regressions based in the VT-Micro model. In the literature, there is no evaluation of the influence of NO_x emission peaks on emission models.

CHAPTER 3

Methodology

This section describes the general methodology for the development of this work. Here, a description of the emission tests is provided, and the common computations or procedures across the analysis of each chapter is detailed. Further, specific methods are described in each chapter.

The entire analysis, data processing and engineering, statistical analysis, and graphics were performed in a well-known open-source software, R (R Core Team, 2019). Also, several packages were used for the tasks required in this study, such as dplyr, tydr, ggplot, caret, randomForest, and e1071. Graphics were edited using open-source, vector image editing software Inkscape (<http://inkscape.org>). For emission modelling, PHEM v13 was kindly provided by TUGraz.

Data from RDE compliant on-road tests were used to perform a descriptive analysis. The descriptive analysis was focused on finding characteristics and relationships between operational data and NO_x emissions. A common first step was to evaluate the environmental performance of the vehicle in the on-road test based on the analysis of the raw distance-specific emission factors for each driving section (urban, rural, and motorway) and total trips.

The first part of the analysis was performed by comparing the cold start and hot-start NO_x emissions for vehicles in Madrid. The tests were conducted using passenger cars with different fuels (gasoline and diesel), powertrains (hybrid and conventional), ignition type (CI, SI: GDI and PFI) and aftertreatments TWC, LNT, and SCR. The NO_x emission level characteristics and the large differences between the hybrid and DI gasoline vehicles were explained via the analysis of tailpipe air-fuel ratios and exhaust gas temperatures recorded from PEMS.

Since diesel vehicles with different aftertreatment technologies have been introduced to accomplish the stringent emission regulations, the next analysis was performed to understand the influence of the high NO_x peaks on the emission factors and the relationship of those NO_x peaks with operational variables. A definition and method to cluster the NO_x peaks were developed based on the representativity of these NO_x peaks in the percentage of total emissions. Datasets with high NO_x emissions were named as high emission sets (HES) and used along with this study. Descriptive computations such as probability density functions, boxplots, and conditional distributions were applied on the HESs and on-road test data.

The SCR systems are the most promising technology for NO_x reduction in CI engines. Therefore, the next step was to analyse in deep the performance and behaviour of this system under real-world conditions. For this objective, the data from RDE tests

performed in Graz with a measurement of NO_x concentrations and exhaust gas temperatures before and after the SCR system was key. The analysis related the SCR performance with power, exhaust mass flow, thermal operating window and NO_x conversion (deNO_x) efficiency. The NO_x peaks were explained by analysing the relationship with the mentioned variables.

The hard task of the NO_x emission modelling was faced in the last part, considering different modelling approaches and the influence of the NO_x peak. The SCR vehicle analysed in the previous chapter was used because of the extensive testing and data necessary for the modelling in PHEM; the data was provided by TUGraz. The HESs were assessed in a physics-based model (PHEM) and by using a machine learning algorithm (random forests). A black-box algorithm was used because the objective was not to provide the best reliable model; however, the objective was to investigate the influence of NO_x peaks, so non-parametric models are the most commonly used methods for addressing non-linear problems (Pan et al., 2019). Unlike the stochastic approach, these models make no prior assumptions about the data distribution. The models were trained or built using real-world data and evaluated in entire RDE trips. The prediction accuracy was evaluated for the entire trips and for the high NO_x emission sets. Finally, conclusions about this thesis and future works paths are proposed.

To ensure that emissions are reflected as recorded in real driving conditions, the high instantaneous NO_x emissions were compared to other parameters without smoothing, elimination of outliers, or segregation of the data (O'Driscoll et al., 2018, 2016). Therefore, the RDE sections were discretised based on speed bins only for the verification of overall trip dynamics, as established in Appendix 7a of Reg. (UE) 2017/1151 regulation (EC, 2017). This verification guarantees that RDE tests are within regulations and reflect “normal” European driving, as demonstrated in (Gallus et al., 2017). See Annex A. for a detailed comparison of RDE tests and regulations.

3.1. Analysed parameters

(Frey et al., 2010) classified the explanatory variables for emission modelling as internally observable variables (IOVs) such as engine speed, air intake pressure, and others. The other type of variables were called externally observable variables (EOVs) such as speed, acceleration, and road grade. In modern vehicles, the aftertreatments have a strong influence on the emissions at the tailpipe, and their operational variables are used as determinants for emission analysis and modelling. These variables are exhaust gas temperature at the inlet of the aftertreatment device, space velocity in aftertreatment, monolith temperature, etc. Therefore, in this study, those variables are also considered IOVs.

The instantaneous data of the analysed parameters were derived from PEMS. In this study, the variables related to emissions, in particular with NO_x , were linked to vehicle and engine operating conditions and/or driving severity (**Figure 3.1**). Those variables were analysed through the study to understand the high NO_x emissions characteristics

and phenomena. First, acceleration, speed and road grade characterise vehicle operating conditions, and their variability mainly depends on traffic conditions and road infrastructure. However, engine speed, exhaust gas temperature, and air-fuel ratio characterise engine operating conditions, and both set of parameters are determinant for aftertreatment operations; their variability depends on engine type, fuel, engine control strategies, among other factors.

To correctly correlate NO_x emissions with the tailpipe exhaust gas temperatures and air-fuel ratios, only the periods with exhaust gas flow were analysed. During the engine-off periods, no gas flow occurs.

Figure 3.1. Relationship between operating conditions and analysed parameters for emission analysis and modelling

Vehicle and engine operating conditions are not independent, and they are both interrelated with the driving style. Driving style was analysed using different driving parameters such as RPA, mean a^+ , $v \cdot a^+$, and engine speed (Fonseca González et al., 2010; Franco et al., 2014; Gallus et al., 2017). With respect to normal driving, aggressive driving increases the demand for engine power as it requires increased engine speed, and this leads to increased acceleration and speed of the vehicle. Similarly, driving severity increases the demand for engine power due to an “aggressive” speed-time profile.

3.2. Emission tests description

This study is an extensive analysis of NO_x emissions from previously measured data in the laboratory and from real driving emission tests performed in the cities of Madrid (Spain) and Graz (Austria). The tests were conducted with Euro 6b passenger cars, following the main prescriptions of the RDE regulation (EC, 2017).

3.2.1. Tests in Madrid, Spain

The data from this measurement campaign were used for the investigations in Chapters 4 and 5.

3.2.1.1. Test routes

The tested vehicles were driven over two real-world routes in Madrid city and its surroundings, with different objectives: an urban warming-up test route to observe the cold start and early warmed-up emissions, and an RDE test route to know the overall

environmental performance of the vehicles under hot-start driving. One professional driver tested all vehicles to reduce the influence of driving style on the tests. Similar traffic conditions were intended between tests; therefore, the tests were conducted on weekdays, during off-peak traffic periods in the morning and afternoon. The tests were performed in May–July (spring–summer), with an average ambient temperature of 24.3 °C (s.d. 4.1). **Figure 3.2** shows the trace of the routes, and **Table 3.1** summarises the main parameters. The detailed comparison of this study and the requirements of RDE regulation are provided in Annex A.

a)

b)

Figure 3.2. Test routes traces in Madrid (a) warming-up test route (b) hot-start RDE test route, warming-up test route (in green). Source (Mera et al., 2019)

Warming-up route

The warming-up route comprised of an urban closed loop around the Universidad Politécnica de Madrid (UPM) South Campus (**Figure 3.2**). According to the regulation Reg. (EU) 2017/1154, the preconditioning time for cold start testing is more than 6 hours. Therefore, every warming-up test was conducted in the morning before the performance of several hot-start RDE tests. The cold start lasted the first five minutes ($t \leq 5$ min) of driving, which is the duration period established by RDE regulation unless the coolant temperature can be reliably determined, in which case the cold start period ends when the coolant attains 343 K (70 °C). The instantaneous coolant temperature was not properly recorded from the OBD port during the tests. For the HEV, the cold start period began with the first combustion-engine start, and it lasted 5 min of driving. For all vehicles, the hot running (HR) period covered the consecutive five minutes ($5 < t \leq 10$ min) to the cold start.

During the warming-up tests, long vehicle stop periods were minimised to observe the uninterrupted warm-up behaviour of the vehicles in urban conditions. Therefore, the warming-up test route had no traffic lights or heavy congestion, where vehicles equipped with stop-start systems would spend much time in engine-off periods. Instead, this public route included several crosswalks with speed reducers.

RDE route

After the warming-up driving, the vehicles performed several hot-start RDE tests in a unique route. These tests complied with the main RDE regulations of Reg. (EU) 1151/2017. One RDE trip had a total distance of 76.5 km, and its urban, rural, and motorway sections were formed of 30 %, 38 %, and 32 % of the total route, respectively. The minimum altitude of the route was 519 m above sea level. During RDE tests, the cumulative positive altitude gain for the entire trip was 828 m /100 km. Some tests result exceeded RDE regulation boundaries. In the measurement campaign, one section of one test surpassed the dynamic driving parameter, and two tests had a stop period up to 34 % in the urban section, while regulation establishes a limit of 30 %. However, all tests during the campaign were used to reflect real-world driving with more data. **Figure 3.3** shows an example of the speed-time profile of the testing routes. The figure shows that vehicle stop periods were not present during warming-up trips.

Figure 3.3. Speed-time profile example for warming up and RDE routes. Cold start (CS), hot running (HR).

Table 3.1. Parameters of Madrid test routes

Parameter		Warming up		RDE			
		Cold start (CS)	Hot running (HR)	Urban	Rural	Motorway	Total
Testing time	[min]	5	5	60.8 (3.5)	26.3 (1.0)	14.2 (1.1)	101.2 (4.2)
Distance	[km]	2.4 (0.29)	2.4 (0.28)	23.2	28.8	24.5	76.5
Average speed	[km h ⁻¹]	28.3 (3.4)	30.1 (2.0)	23.0 (1.3)	65.9 (2.3)	104.2 (6.5)	45.4 (1.8)
RPA	[m s ⁻²]	0.22 (0.03)	0.21 (0.04)	0.25 (0.03)	0.19 (0.01)	0.13 (0.01)	0.19 (0.01)

Values in the table present average and (standard deviation) of all tests. RPA – Relative positive acceleration. The number of tests performed per vehicle is shown in **Table 3.2**

3.2.1.2. Tested vehicles

The tested vehicles were five Euro-6b SUV vehicles fuelled by gasoline or diesel, with different NO_x aftertreatment systems; none of the aftertreatments had active heating systems. The HEV had only one TWC close-coupled to the engine. The vehicles had manual gearboxes and turbochargers, except for the HEV that had a parallel-series (full) hybrid configuration and atmospheric air intake. The detailed characteristics of the vehicles are shown in **Table 3.2**. The stop-start system of the G-DI vehicle was intentionally deactivated to measure the exhaust gas temperature without the cooling effect on the TWC produced by the stop-start system. Thus, the opposite stop-start behaviours of TWC systems of the HEV and G-DI vehicles could be compared.

Table 3.2. Characteristics of tested vehicles in Madrid

ID	Fuel	Model year	Engine size [L]	Engine power rated [kW]	Fuel injection type	NO _x control	Stop-start system	Curb weight [kg]	Mileage [km]	Warming-up tests	RDE tests
G-DI	Gasoline	2016	1.2	96	Direct injection (stratified air-fuel mixture)	TWC	Yes*	1381	5400	1	3
G-HEV	Gasoline	2017	2.5	114 [#]	Port-fuel injection (PFI)	TWC	–	1810	13600	3	5
D-SCR	Diesel	2016	2.0	110	CRDI	EGR + SCR + ASC	Yes	1560	8300	2	5
D-LNT	Diesel	2017	1.6	88	CRDI	EGR + LNT	Yes	1615	6000	2	5
D-EGR	Diesel	2017	2.0	100	CRDI	EGR	Yes	1604	1600	2	5

Power only for the combustion engine, * System deactivated. ASC = Ammonia slip catalyst. CRDI = Common-rail diesel injection

3.2.1.3. PEMS

The MIVECO-PEMS was developed and validated by the Universidad Politécnica de Madrid (Casanova and Fonseca, 2013; Fonseca González, 2012). For this measurement campaign, the system was simplified to decrease its weight and size, and only NO_x

emissions were measured. Further, this system was used in the study of high instantaneous NO_x emissions by (Mera et al., 2019b), with a sampling frequency of 10 Hz for the measured parameters. The PEMS consists of a pitot-type exhaust flow meter (EFM) (Fonseca González et al., 2016), a direct-installation Horiba Mexa 720 ceramic zirconium NO_x sensor, a relative air-fuel ratio (λ) meter, exhaust gas temperature sensors, a global positioning system (GPS), and a weather station to record ambient temperature and humidity. The NO_x sensor measured concentration directly in the exhaust line at the EFM level, with an accuracy of ± 30 ppm NO_x (0–1000 ppm), ± 3 % (1001–2000 ppm), and ± 5 % (2001–3000 ppm). This device is electrically heated at the internal operating temperature. The relative air-fuel ratio was measured using an ETAS LA4 wide-range lambda meter with a measurement range of $\lambda = 0.7$ –32.77 and an accuracy of ± 1.5 %.

In addition, vehicle and engine speeds were recorded from the OBD port of the vehicle. The temperature of the aftertreatments could not be easily measured directly or recorded via OBD. Therefore, the exhaust gas temperature was measured at the tailpipe, in the EFM, using K-type thermocouples with a measurement range of 0–300 °C. Approximately 190 kg was added to the mass of the vehicle, including the PEMS system, driver, co-driver, and the batteries, which were the power source for the PEMS. The recorded data were checked and synchronised in the post-processing stage. The synchronisation was conducted via cross-correlation, and the results were manually checked to ensure correct alignment.

The values of the measured exhaust gas temperature were references for the aftertreatment temperature and they varied among vehicles because they were measured in the EFM at the tailpipe. This temperature did not correspond to the actual monolith catalyst temperature. This implies that every PEMS installation had unique measurement values because of the heat losses in the exhaust system. Additionally, the thermal inertia of aftertreatment elements affected the instantaneous gas temperature values at the tailpipe. However, these measurements reflected the general state of aftertreatment systems through heat transfer from exhaust gases. To capture the average values, the computations were not treated as instantaneous. For all vehicles, the computations of average exhaust gas temperatures were performed by removing the engine-off periods. This would minimise the error of using the exhaust gas temperature as a proxy of that of the aftertreatment.

3.2.2. Tests in Graz, Austria

The data from these on-road tests were used for the investigations of Chapters 6 and 7.

3.2.2.1. Test route

Three tests were performed following the main prescriptions of RDE regulation Reg. (EU) 2017/1151, within a route that covers the city and the surroundings of Graz, Austria, as shown in **Figure 3.4**. This study examines the data from normal-driving hot-start RDE tests. The cold start was not analysed; therefore, the cold-start segment test was removed, according to the RDE regulation. The RDE tests were carried out in an ambient temperature range of 14–22 °C, resulting in 217 min of measurements, and with trips of 84.1–87.7 km, and actual in urban sections of 11.7–14.6 km. According to the RDE regulation, the cumulative positive altitude gain for the entire trip was 860–881 m per 100 km, and for the urban section 1039–1093 m per 100 km. The information of the parameters for these tests are listed in **Table 3.3**, and the detailed comparison of this study and the requirements of RDE regulation are provided in Annex A.

Table 3.3. Parameters of Graz test route

		Urban	Total
Testing time	[min]	45.6 (s.d. 6.1)	106.1 (s.d. 4.9)
Distance	[km]	12.9 (s.d. 1.5)	85.7 (s.d. 1.9)
Average speed	[km h ⁻¹]	17.2 (s.d. 2.5)	48.5 (s.d. 2.7)
RPA	[m s ⁻²]	0.23 (s.d. 0.03)	0.18 (s.d. 0.01)

Table shows the mean and standard deviation (s.d.) of all performed tests.

Figure 3.4. Test route traces in Graz. The urban section consisted of two parts at the beginning and at the end of the trip.

3.2.2.2. Tested vehicle

Investigations were performed in one diesel passenger car, homologated under the Euro 6b regulation. The car represents a typical class E vehicle from the European market, and it was fuelled with standard diesel B7. In addition, the stop-start system was not activated. Detailed specifications are summarised in **Table 3.4**. The vehicle measurements were funded by Umweltbundesamt Germany in the course of the project “Field Monitoring of Vehicles and Updating of Handbook of Emission Factors for Road Transport” (Matzer et al., 2019)

Table 3.4. Characteristics of tested vehicles in Graz

Fuel	-	Diesel
Displacement	[L]	2.0
Engine power	[kW]	140
Engine type	-	CRDI + VGT
Aftertreatment	-	DOC + SCR* + DPF + ASC
Type approval NO _x emissions (NEDC)	[mg km ⁻¹]	58.5
Transmission	-	6-speed AT
Curb weight	[kg]	1607
Mileage	[km]	~17000

*close-coupled location. DOC = Diesel oxidation catalyst, DPF = Diesel particle filter. VGT = Variable geometry turbocharger.

3.2.2.3. PEMS

The real-driving NO_x emissions were measured using an AVL MOVE PEMS system at a 1 Hz sampling time. This device has a non-dispersive ultraviolet analyser (NDUV) for NO_x concentrations and non-dispersive infrared analyser (NDIR) to measure CO₂ concentration. The EFM is a differential pressure Pitot type device. Further, the PEMS recorded vehicle position and speed using a GPS system combined with a meteorological station for the air ambient parameters such as barometric pressure, temperature and humidity.

Figure 3.5. Schematic layout of the exhaust system of the test vehicle and the measurement points of emissions and exhaust gas temperatures. EGR system is not plotted

Figure 3.5 shows the layout of the exhaust system with the main elements and the measurement points. The exhaust gas temperatures along the exhaust system, NO_x concentration upstream of SCR, vehicle and engine speeds, and engine coolant temperature were recorded via the OBD port using the so-called VAG-COM Diagnosis

System (VCDS). The exhaust gas temperatures were measured at the following points: before turbocharger (engine out), between turbocharger and DOC, between DOC and SCR-DPF, and after the SCR-DPF. The temperature after the DOC (DOC downstream) is assumed as the entering temperature to SCR (SCR-inlet) owing to the short-tube connection (150 mm) between these points, only small differences of temperature are expected.

The measuring equipment used independent batteries as the power source, to avoid the influence on emissions produced by the energy consumption in the electric system of the vehicle. The weight added by the PEMS system, batteries and components was 84 kg. Considering the driver and co-driver of 150 kg, the total testing weight for the vehicle was 1868 kg.

3.3. General computations

3.3.1. Emissions-related computations

3.3.1.1. Cumulated NO_x emissions

Instantaneous NO_x emissions (mg s^{-1}) were obtained from the instantaneous exhaust gas flow and instantaneous NO_x concentration, which were measured by the exhaust flow meter and the gas analysers, respectively. The cumulated NO_x emissions (mg) is the integral of the instantaneous emissions over time, and it represents the total mass of NO_x emitted. The cumulated emissions of the pollutant j for any dataset are given as:

$$m_j = \sum_n \dot{m}_j \cdot \Delta t \quad (3.1)$$

where $\dot{m}$ is the instantaneous mass emission (mg s^{-1}) of each observation, n is the number of observations of the dataset and Δt is the sampling time, equal to 0.1 s and 1 s for the tests in Madrid and Graz, respectively.

3.3.1.2. Emission factors

According to RDE regulation (EC, 2017), the emission factors of RDE tests are analysed using the moving averaging window (MAW) and power binning (PB) methods. However, in this study, as the objective was to analyse the emissions as were produced, the raw distance-specific emission factors ($\text{mg NO}_x \text{ km}^{-1}$) for vehicle i , pollutant j , and section k were computed as:

$$EF_{i,j,k} = \frac{\sum \dot{m}_{i,j,k} \cdot \Delta t}{s_{i,j,k}} \quad (3.2)$$

where $\dot{m}$ is the instantaneous mass of emission (mg s^{-1}) produced for a distance s (km).

3.3.1.3. Deviation ratio

To compare the NO_x emission levels of section k with respect to regulations, the dimensionless term deviation ratio (DR) was used (O'Driscoll et al., 2016; Thompson et al., 2014; Weiss et al., 2012, 2011a)

$$DR_{i,k} = \frac{EF_{i,k}}{ES} \quad (3.3)$$

where, ES is the emission standard limit of 60 and 80 mg NO_x km⁻¹ imposed for Euro 6 gasoline and diesel vehicles, respectively.

3.3.1.4. deNO_x

The percentage of instantaneous NO_x reduction between the upstream and downstream of the aftertreatment device was computed as:

$$deNO_x = 100 \cdot \frac{NO_{x,up} - NO_{x,down}}{NO_{x,up}} \quad (3.4)$$

3.3.1.5. Determination of High NO_x emissions sets (HESs)

An “high” emissions set (HES) was first developed in (Mera et al., 2019b), and it is defined as the set of observations: a) with the highest instantaneous tailpipe NO_x emission of a test or section; b) that is above a NO_x threshold (h); c) that represents a certain amount of total emissions. To determine the HESs, the instantaneous tailpipe NO_x emissions are sorted in decreasing order; then, the cumulated emissions are computed starting from the maximum instantaneous NO_x emission until the desired percentage of total emissions is reached. It can be obtained by solving

$$\int_{max}^{h_L} NO_x dt = L \cdot \int_0^T NO_x dt \quad (3.5)$$

where, h_L is the NO_x threshold as the searched parameter (g s⁻¹), L is the fraction of total emissions, and T is the total time of the analysed section or dataset. The integral in the left side is computed over the ordered instantaneous NO_x emissions from the highest to the lowest values.

For instance, as shown in **Figure 3.6** for the measurements in Madrid, HES-20 represents the set of observations with the highest instantaneous NO_x emissions, whose cumulated emissions are 20 % NO_x of the total emissions. This corresponded to instantaneous NO_x emissions over the threshold (h_{20}) of 88.8, 66.2, and 21.3 mg s⁻¹ for EGR, LNT, and SCR diesel vehicles, respectively; in addition, it corresponded to 1.5, 1.6, and 0.7 % of the total time, respectively.

Figure 3.6. Determination of HESs. The area under the curve represents 20 % and 50 % of cumulative NO_x emissions, respectively. The areas are trimmed at the top to improve visualisation. Source (Mera et al., 2019b)

3.3.1.6. Correction of ammonia cross sensitivity on NO_x sensor

Cross sensitivity was corrected for the NO_x sensor used in the Madrid tests. While NO is primarily formed during combustion, ammonia (NH₃) is a secondary pollutant formed in some catalytic converter systems (Heeb et al., 2008). The ammonia cross sensitivity is present in zirconium NO_x sensors and has been primarily analysed to control SCR systems (Aliramezani et al., 2016; Bonfils et al., 2014; Frobert et al., 2013; Zhang et al., 2015). The cross sensitivity of NO_x sensors is primarily caused by NH₃ oxidation in the first chamber of the sensor (in the sensor oxygen pump) which results in N₂O, NO, and NO₂. These gases pass to another chamber where NO and NO₂ are measured together with the original NO_x emissions (Aliramezani, 2019).

Gasoline vehicles

The ammonia cross-sensitivity was corrected by removing NO_x measurements under rich combustion, i.e., $\lambda < 1$, as determined using the PEMS lambda sensor. NH₃ is formed in TWCs under rich conditions when the catalyst light-off temperature is attained (Heeb et al., 2008; Suarez-Bertoa et al., 2017). In particular, NH₃ emissions are higher under high vehicle power demand with rich air-fuel ratios (Huai et al., 2003; Livingston et al., 2009; Suarez-Bertoa et al., 2014). NO and NH₃ emissions of TWC vehicles are anticorrelated. The operation of TWC under rich conditions enables optimal NO conversion; however, it forces the release of NH₃. Under lean conditions, NH₃ is not formed, but the de-NO_x efficiency of TWC decreases (Heeb et al., 2008; Huai et al., 2003).

Diesel vehicles

The ammonia was not corrected for the diesel vehicles, because it is produced primarily by SCR-equipped vehicles, and it is controlled by the ammonia slip catalyst (ASC). A marginal influence of NH₃ cross sensitivity on the D-SCR tested vehicle was assumed. Studies have indicated low NH₃ emissions for Euro 6b ASC-equipped diesel vehicles. For example, a maximum value of 1 mg NH₃ km⁻¹ was reported for a diesel vehicle under real

driving tests (Suarez-Bertoa et al., 2020). For a vehicle retrofitted with SCR and NH_3 anti-slip coating, reported no NH_3 emissions (Giechaskiel et al., 2019)..

3.3.2. Vehicle and engine activity

3.3.2.1. Vehicle stop and engine-off periods

The engine-off periods were defined as observations with engine speed < 50 rpm. For HEVs, these engine-off periods are produced by hybrid system management. In contrast, the engine-off periods of conventional vehicles may occur by the action of the stop-start system.

To compute the vehicle stopping time, the stop periods were defined as observations with vehicle speed $< 1 \text{ km h}^{-1}$. During the tests in Madrid, the driver ensured that the stop-start system was not deactivated, e.g. by depressing the clutch pedal during stops.

3.3.2.2. Driving mode

The driving modes were computed according to the speed and acceleration data listed in **Table 3.5**.

Table 3.5. Driving modes definition

Mode	Speed [km h ⁻¹]	Acceleration [m s ⁻²]
Idle	$v < 1$	-
Cruise	$v \geq 1$	$-0.1 \geq a \leq 0.1$
Acceleration	$v \geq 1$	$a > 0.1$
Deceleration	$v \geq 1$	$a < -0.1$

3.3.2.3. Vehicle specific power (VSP)

Power wheel represents the instantaneous power delivered by the engine to change the kinetic and potential energies of the vehicle to overcome rolling resistance and aerodynamic drag. As a mass-independent parameter, it is widely used as vehicle specific power (VSP), in W kg^{-1} . The VSP has been used in several studies of fuel consumption and emissions in Europe (Duarte et al., 2015; Faria et al., 2018; Varella et al., 2017) and in emission models, such as MOfor Vehicle Emission Simulator (MOVES) from the US Environmental Protection Agency (EPA). The VSP is formulated as (Frey et al., 2010; Jiménez-Palacios, 1999):

$$VSP = \frac{P_{wheel}}{m} = v \cdot (a(1 + \varepsilon_i) + g \cdot \alpha + g \cdot C_R) + \frac{1}{2} \rho_a \cdot v^3 \left(\frac{C_D \cdot A}{m} \right) \quad (3.6)$$

where, m corresponds to the vehicle mass, v is the vehicle speed (m s^{-1}), a is the acceleration (m s^{-2}), $\varepsilon_i \sim 0.1$ is the mass factor for the rotational masses, $g = 9.81 \text{ m s}^{-2}$ is the acceleration due to gravity, α is the road grade, C_R is the rolling resistance coefficient (dimensionless), C_D is the drag coefficient (dimensionless), ρ_a is the air density (1.207 kg m^{-3} at 20°C) and A is the cross-sectional area (m^2).

To compute VSP for the tested vehicles in Madrid, a generic value ($C_R = 0.0135$) for passenger cars were used (Jiménez-Palacios, 1999). A and C_D were sought in general characteristics of the vehicles from the literature. In the case of the tested vehicle in Graz, the rolling resistance coefficients were derived from the tire label. Thus, $C_R = (F_{r0} + F_{r1} \cdot v)$, where $F_{r0} = 9.5 \times 10^{-3}$ (dimensionless) and $F_{r1} = 7.5 \times 10^{-5} \text{ s m}^{-1}$. The other sought parameters are $A = 2.29 \text{ m}^2$ and $C_D = 0.319$, which were derived from a literature study performed by TUGraz team.

VSP usually is divided in 14 modes that represent the use of power during driving, where each mode has statistically different fuel consumption values, and none of them is dominant in the estimation of the trip total fuel consumption (Frey et al., 2002; Varella et al., 2019, 2017, 2016). The following table shows the VSP mode and derived power usage.

Table 3.6. VSP power usage level and mode

#	VSP mode [W kg ⁻¹]	Power usage	VSP range [W kg ⁻¹]
1	VSP < -2	Deceleration	VSP < 0
2	-2 ≤ VSP < 0		
3	0 ≤ VSP < 1	Idle	0 ≤ VSP < 1
4	1 ≤ VSP < 4	Normal usage-low power	1 ≤ VSP < 10
5	4 ≤ VSP < 7		
6	7 ≤ VSP < 10		
7	10 ≤ VSP < 13	Normal usage-high power	10 ≤ VSP < 19
8	13 ≤ VSP < 16		
9	16 ≤ VSP < 19		
10	19 ≤ VSP < 23	Extra-high power	VSP ≥ 19
11	23 ≤ VSP < 28		
12	28 ≤ VSP < 33		
13	33 ≤ VSP < 39		
14	VSP ≥ 39		

3.3.3. PHEM modelling and validation

The vehicle and tests from Graz were simulated in PHEM v13. This micro-level emission model uses the longitudinal dynamics and engine emission maps for the estimation of fuel consumption and emissions to estimate every driving condition (Weller et al., 2019). Therefore, engine-out NO_x emissions are resultants from the simulation of the RDE tests' vehicle dynamics, i.e. velocity, gradient and engine speed at 1 Hz resolution. In the case of SCR vehicles, PHEM estimates the tailpipe NO_x emissions in a sub-model that creates maps for the SCR's deNO_x, based on gas temperature and space velocity. For the computation of components and exhaust gas temperatures along the exhaust system, PHEM runs a detailed 0-d transient heat transfer model (Rexeis, 2009). The modelling methodology in PHEM is depicted in **Figure 3.7**.

Figure 3.7. Schematic methodology of PHEM

For the tested vehicle, the wide range of parameters for the PHEM modelling and simulation were measured or obtained by TUGraz team in past investigations, and the model, emission maps and SCR conversion maps were calibrated on test data; therefore, a high accuracy and meaningful precision were expected. After the modelling, the model was validated by comparing the real-world CO₂ and NO_x emissions with the simulation results of the built PHEM model. In particular, the high accuracy of CO₂ emissions indicates correct modelling and simulation.

3.3.4. Error metrics

The metrics to assess the accuracy of the estimations of PHEM and the other models were (a) emission factor error (EFE), which is equivalent to the total error; (b) root-mean-square error (RMSE); and (c) the coefficient of determination (R²), which are computed as

$$EFE = \frac{EF_{predicted} - EF_{actual}}{EF_{actual}} \quad (3.7)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_i - \hat{y}_i)^2} \quad (3.8)$$

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (3.9)$$

where, y_i and $\hat{y}_i$ represent the actual and estimated instantaneous emission, $\bar{y}$ is the median, and N is the number of observations of the data.

The RMSE shows sensitivities to outliers and larger values. Therefore, it was selected to assess the accuracy of instantaneous NO_x predictions because of the importance of emission peaks on total emissions. When the EFE error was averaged, it was performed using absolute values because EFE could be negative or positive. An average over non-absolute values could lead to low average EFE error.

3.3.5. Machine learning modelling

The general process to train a machine learning model and to obtain the final model is described in **Figure 3.8**. The overall process was performed in R (R Core Team, 2019) and the model training using caret package (Kuhn, 2008), which provides only one environment for training, tuning and validation of the models. Each algorithm has its own fitting algorithms; however, machine learning algorithms tend to overfit. To avoid overfitting, the validation process is an important step that, in practice, is performed by the tuning the user model parameters (hyperparameters). For this study, the k-fold repeated cross validation process was used. Here, the main idea behind cross-validation is that each sample in our dataset has the opportunity of being tested. k-fold cross-validation is a special case of cross-validation that iterates over a dataset set k times. In each round, the dataset is split into k parts: one part is used for validation, and the remaining k-1 parts are merged into a training subset for model evaluation (Raschka, 2018). The ML models have important parameters that cannot be directly estimated from the data and are tuned by the user. The model was tuned using grid search to obtain the entire behaviour of the model for the evaluated hyperparameters. The final model, which contains the best hyperparameters, is tested using the error metrics on the remaining testing trip. This process is repeated to test every RDE trip based on training on the other two RDE trips.

Figure 3.8. General process to train and to tune a machine learning model

During the training and tuning, a feature selection process can be applied to obtain a model with more informative predictors. It simplifies and reduces the model; in addition, it allows to understand what predictors work better in the selected ML algorithm, although the accuracy can be reduced. In this study, the variable importance analysis was

performed at the end of the process to observe the importance of the predictors on the models. Variable importance estimates an overall quantification of the relationship between the predictor and outcome. For RF, the variable importance is computed in caret, as stated in the R package: “For regression, the MSE is computed on the out-of-bag data for each tree, and then the same computed after permuting a variable. The differences are averaged and normalized by the standard error. If the standard error is equal to 0 for a variable, the division is not done”.

CHAPTER 4

Cold start and hot-start NO_x emission levels. Influence of exhaust gas temperature and air-fuel ratio on aftertreatment performance

4.1. Similarity of the tests performed in Madrid

Figure 4.1 compares the power demand between warming up, urban, rural and motorway sections of the RDE tests. The figure illustrates similar VSP profiles between the same sections and vehicles. However, close to VSP = 0, the observable differences in the probability density functions (PDF) between the warming-up and urban trips were due to the minimization of stop periods during the warming-up route. These minimum stop-periods let to measure a continuous “warming-up” of exhaust gas temperature and to prevent variability between these short test trips. Cold start (CS) and hot running (HR) testing sections were directly comparable. They were performed under the same testing conditions, i.e. the same urban closed-loop route and similar driving parameters such as average speed and RPA.

Figure 4.1. Probability density functions (PDF) of vehicle specific power (VSP) for warming-up, urban and motorway routes. The figure shows all trips of the measurement campaign.

4.2. Vehicle and engine activity

Table 4.1 reflects that the vehicle stop periods were only relevant in the urban sections of the RDE tests, and they were similar for all vehicles, namely, at an average of 28 % (s.d. 2.3 %). In contrast, rural and motorway stop periods can be considered negligible.

Table 4.1. Percentage of time of vehicle stop periods (t_{stop}) and engine off periods (t_{off}) for each route and test section.

	Warming up				RDE					
	Cold start		Hot-running		Urban		Rural		Motorway	
	t_{stop} [%]	t_{off} [%]	t_{stop} [%]	t_{off} [%]	t_{stop} [%]	t_{off} [%]	t_{stop} [%]	t_{off} [%]	t_{stop} [%]	t_{off} [%]
G-DI	0	0	1	0	32	0	2	0	1	0
G-HEV	0	46	0	57	27	72	3	22	0	1
D-SCR	4	0	0	0	26	19	2	1	0	0
D-LNT	6	0	5	1	28	20	3	2	0	0
D-EGR	5	0	3	0	28	19	3	0	0	0

Values represent average between tests

Owing to the stop-start action, engine-off periods (t_{off}) are very similar to stop periods for conventional vehicles with stop-start systems activated. However, this is not always applicable to HEV vehicles, where the hybrid system controls the engine switch-on via its complex strategy for energy recovery and demand. For the tested hybrid vehicle, engine-off periods were larger than stop periods. The difference that represented the time the vehicle was running with the engine off can be computed using

$$t_{running,ICE\ off} = t_{off} - t_{stop} \quad (4.1)$$

This parameter for the HEV vehicle was consistent in urban conditions, considering that the warming-up route had minimal stop periods. The parameter accounted for approximately half of the time (45–57 %) during the CS, HR and urban sections. This is important for urban air quality because, during these engine-off periods, the hybrid vehicle was in electric mode, so emissions were not released. In the rural section, $t_{running,ICE\ off}$ was approximately one-fifth (19 %) of the time, while in motorway section the engine was turned off during a negligible time (1 %). Through the action of the stop-start system (without gas flow), catalysts lose heat by natural convection, radiation, and conduction to exhaust elements; however, for long engine-off spans of HEVs, forced convection appears during $t_{running,ICE\ off}$, increasing heat losses. Therefore, the thermal management of TWCs in hybrid vehicles is important for urban and rural driving. For conventional vehicles, the urban engine-off periods were equivalent to those of the hybrid vehicle in the rural sections, which stress the importance of the thermal management of the aftertreatments.

4.3. Warming up profiles

Figure 4.2 shows the exhaust gas temperature, NO_x emissions and engine on-off profiles of the warming-up tests. The measurements of only one trip were plotted; the other trips had comparable patterns and are not included for the clarity of the figure. An uninterrupted warm-up is reflected for all vehicles, except for the HEV, which had several engine-off periods. All five vehicles presented the expected general pattern of increasing exhaust temperature with time over the 10-min of the warming-up test. However, the exhaust gas temperature of the hybrid and G-DI vehicles exhibited a more

noticeable saw profile with temperature drops. The exhaust gas temperatures in spark-ignition (SI) engines were higher than in compression-ignition (CI) engines, so the change in exhaust gas temperature of the gasoline vehicles was more visible. For the hybrid vehicle, with no-heated TWC, engine-off periods (red line in **Figure 4.2**) represented 51 % of the warming-up drive time. This implied low heat transfer for the TWC from exhaust gases. For no-heated catalysts, vehicles often accelerate the heating up of catalysts via controlling operational engine parameters such as valve timing, air-fuel ratios, and the start of combustion delay (Gao et al., 2019b). These strategies can improve the light-off catalyst but deteriorates the engine efficiency.

Figure 4.2. Tailpipe exhaust gas temperature and NO_x concentration profiles during warming-up tests: cold start (CS), i.e. $t \leq 300$ s; and hot-running (HR) tests, i.e. $300 < t \leq 600$ s.

The figure shows a clear decrease in NO_x emissions in approximately 50 s for the HEV and 180 s for the D-SCR vehicle, which reflects the light-off of the catalysts. In conventional vehicles, (Zhao and Winterbone, 1993) reported light-off temperatures being attained in 210 s in a wide-open throttle scenario, extended to 555 s in an idling scenario. However, the fast light-off in the G-HEV vehicle can be explained by the increased load of the HEV engine during cold start, which according to (Gong et al., 2011), led to a lower fuel penalty and faster increase in temperature. In (Miao et al., 2009) light-off times of 232 s in an SCR device was reported, with estimated light-off times of 170 s, owing to the thermal inertia reduction of DOC and pipe connection in a 43 %, or using electrical heating for the SCR, with a power of 4.85 kW.

4.4. Distance-specific emission factors

Figure 4.3 shows the average NO_x emission factors for each warming-up and RDE section; horizontal lines represent Euro 6 emission limits. This figure illustrates that all vehicles had cold start emissions (in blue) above Euro 6 limits. In the other sections of the tests, G-HEV and D-SCR vehicles exhibited lower emissions than cold start section, but this was not the case for the other vehicles. The CS emission factors of the G-HEV and D-SCR vehicles were 1.1 and 2.7 times the Euro 6 limits, respectively. Cold start emissions were similar between fuel type while in the other testing sections, every vehicle had different emission levels. These results reflected the low efficiency of aftertreatments under those conditions. G-DI and G-HEV vehicles averaged 86 and 64 mg NO_x km⁻¹, respectively. The diesel vehicles had comparable emission levels, averaging 214 (s.d. 50.1), 158 (s.d. 99.5), and 262 (s.d. 191.3) mg NO_x km⁻¹ for SCR, LNT, and EGR-

only (without catalytic aftertreatment) vehicles, respectively. Compared with the EGR-only vehicle and other sections, the emissions levels demonstrated that SCR did not fully operate during cold start. (Suarez-Bertoa et al., 2017) reported higher on-road NO_x cold start emissions of $312 \pm 98 \text{ mg km}^{-1}$ for a Euro 6b diesel vehicle with SCR. The D-LNT vehicle exhibited lower cold-start emissions than the other diesel vehicles did; this can be explained by the possible adsorption of NO during the cold start phase. Contrary to the SCR device, which requires a minimum temperature threshold for urea injection, LNT can operate at lower temperatures.

Figure 4.3. Average emission factors of CS, HR, and RDE tests. Error segments represent ± 1 standard deviation. Euro 6 limits for gasoline and diesel passenger cars are 60 and 80 $\text{mg NO}_x \text{ km}^{-1}$, respectively.

Comparing CS and HR periods, HR emissions levels of G-HEV and D-SCR vehicles were remarkably lower than cold start by 92 and 66 %, respectively. Therefore, the HR emissions for G-HEV and D-SCR vehicles were 0.1 and 0.9 times the Euro 6 limits. Thus, their HR emissions were below Euro 6 limits in the time established by European regulation as cold start, namely, 5 min. The difference in emission levels between CS and HR sections meant that the light-off temperature of TWC and SCR were indeed attained during warming-up, even though the HEV operated with the engine off 51 % of the time. Although the G-HEV had engine-off periods, the light-off of the TWC with the evident reduction in emissions can be explained because the exhaust gas temperatures of SI engines are higher than CI engines (Gao et al., 2019b).

G-DI, D-LNT, and D-EGR vehicles exhibited HR emission factors higher than in the CS section. For the diesel cars, this can be physically explained by late fuel injection and the corresponding increase in exhaust gas temperature combustion during warming-up. This decreased NO_x production from the engine at the beginning of the cold start period.

For the G-DI engine, an HR air-fuel mixture poorer than for the CS occurred during warm-up, which increased NO_x emissions of the HR section by reducing TWC conversion.

The G-DI, D-LNT, and D-EGR vehicles exhibited opposite patterns to the G-HEV and D-SCR vehicles in the emission factor values. First, in the urban driving tests, emission factors levels of G-DI, D-LNT, and D-EGR were CS < HR < urban-RDE while the emissions of the other vehicles were CS > HR ≥ urban-RDE. Second, for the G-DI, D-LNT, and D-EGR vehicles, none of the RDE sections satisfied Euro 6 limits. G-DI, D-LNT, and D-EGR vehicles surpassed these limits in the total RDE tests by 5.0, 7.4, and 9.0 times and in the urban section by 4.9, 6.3, and 4.8 times, respectively. In (Valverde et al., 2019b) diesel Euro 6b vehicles with LNT systems emitted on average two times NO_x of SCR equipped vehicles, which demonstrates the advantage in NO_x conversion of SCR systems. Periods with lean-burn conditions in gasoline direct injection vehicles lead to an increase in NO_x emissions because a TWC operates effectively in stoichiometric and rich air-fuel mixtures (Dardiotis et al., 2013). Recently, high emissions were observed for two GDI Euro-6b vehicles equipped only with TWC (Weber et al., 2019). On the cold-start Artemis urban cycle (André, 2004) at +23 °C, GDI vehicles had in average about 200 mg NO_x km⁻¹, and 278–380 mg NO_x km⁻¹ on the hot-start Helsinki city cycle. Therefore, the emissions of tested G-DI vehicle could be considered as the “upper limit” in the category, and the possible malfunctioning could be rejected by the low mileage of the vehicle. Real-world emissions from Euro 6 GDI vehicles require more investigations for designing effective policies to reduce their possible pollution impacts. Post-Euro-6b GDI vehicles could require lean-burn-like aftertreatments to satisfy emission limits under real-world conditions.

The low NO_x emission levels of the G-HEV vehicle with RDE and urban emission factors of 2.16 (s.d. 1.13) and 1.52 (s.d.1.65) mg km⁻¹, respectively, are notable. These levels confirm the values reported in other studies. Two full hybrid vehicles with similar characteristics, namely, Japan 2009 standard, model 2015 and 2.5 L engine investigated by (Huang et al., 2019) had real driving NO_x emissions in the order of 1–2.5 mg km⁻¹. (O’Driscoll et al., 2018) reported an average urban NO_x emission of 0.002 (s.d. 0.000) mg km⁻¹ for Euro 5 and Euro-6 hybrid electric vehicles. In a study by (Varella et al., 2016), a Euro 5 full-hybrid vehicle released high NO_x under a charge depleting and charge sustaining operation. These conditions increase the power demand to the HEV’s engine.

4.5. Influence of air-fuel ratio on NO_x emissions

4.5.1. Air-fuel ratio levels of gasoline vehicles

Table 4.2 shows the relative air-fuel ratios of the exhaust gas for rich-stoichiometric ($\lambda \leq 1$) and lean ($\lambda > 1$) combustion as measured at the tailpipe. Both selected lambda levels characterise conditions for better and worse NO_x conversion for the TWC, respectively. The computed values indicated that G-DI and G-HEV vehicles had opposite patterns in the air-fuel ratio combustion conditions. The vehicle with direct injection tended to leaner combustion compared with the hybrid vehicle, which had a port-fuel injection

system. During the urban driving, the G-DI vehicle presented $\lambda > 1$ during 95–100 % of the time. The condition of lean combustion decreased to 76 and 60 % of the time for rural and motorway sections. On the contrary, the ICE of the hybrid vehicle operated most of the time in rich or stoichiometric conditions, namely, 81–91 % in the urban drive, 51 % in the rural sections and 55 % in the motorway sections.

Table 4.2. Relative air-fuel ratio (λ) for gasoline vehicles during engine-on periods

	Warming up				RDE					
	Cold start		Hot-running		Urban		Rural		Motorway	
	Rich-st [%]	Lean [%]	Rich-st [%]	Lean [%]	Rich-st [%]	Lean [%]	Rich-st [%]	Lean [%]	Rich-st [%]	Lean [%]
G-DI	2	98	0	100	5	95	24	76	40	60
G-HEV	83	17	81	19	91	9	51	49	55	45

Rich-stoichiometric ($\lambda \leq 1$), Lean ($\lambda > 1$)

4.5.2. Air-fuel ratio values of all vehicles

Figure 4.4 shows the relative air-fuel ratios with different scales for gasoline and diesel vehicles. The figure indicates that the air-fuel ratios of SI engines are richer and narrower than for CI engines. While CI engines remained in lean combustion levels, SI engines operated between rich and lean combustion. For SI engines, this is crucial for TWC performance because the high NO conversion rates of TWC above 95 % during most conditions is possible owing to a lambda control strategy that enables the fast cycling of λ around stoichiometric combustion (Heeb et al., 2008). However, the high NO_x levels reported for the G-DI vehicle can be primarily attributed to the high percentage of time spent operating in slightly-lean conditions. For example, the G-DI engine operated between $1.000 < \lambda \leq 1.075$ the 66 % of the driving time and 38 % of the positive power demand (VSP > 0) conditions. Under slightly-lean conditions, the TWC decreases the NO_x conversion efficiency, and engine-out NO_x emissions are higher by excess in O₂ and high combustion temperatures (Heywood, 1988).

All the vehicles, except the G-DI vehicle in the rural section, show richer cold start air-fuel ratios than HR, urban, and rural sections. During warming-up, a vehicle requires the powertrain and exhaust devices to be heated; hence, enriching of the air-fuel mixture is a method to increase the exhaust temperature and decrease the catalyst light-off time. For this objective, (Gao et al., 2019b) mentioned the use of several techniques such as direct control of the air-fuel mixture; the control of the turbines; and late intake valve opening and early exhaust valve opening for diesel and GDI engines, which both cause post-oxidation and fast catalyst light-off. In this study, the air-fuel ratio of diesel vehicles during cold start exhibited similar values, averaging at a median of $\lambda = 2.161$. The G-DI and G-HEV vehicles had a median of 1.040 and 0.987, respectively. The higher emissions of G-DI in HR with respect to CS could be the result of the reduction in TWC NO_x conversion. The λ values were between 1.005 and 2.214 for the HR sections, while richer values of 0.999–1.929 were measured for CS.

Figure 4.4. Relative air-fuel ratios for warming up and RDE sections, engine-off periods were not considered. Middle bar = median; box height = interquartile range (IQR), IQR = third quartile – first quartile; whiskers = $\pm 1.5 \cdot \text{IQR}$.

Figure 4.4 also shows similar patterns between G-DI and diesel vehicles. Their air-fuel ratios ranged from lean to richer in the following order: urban > rural > motorway. In particular, motorway sections of all vehicles had the richest air-fuel ratios owing to higher and constant power demand. The richer conditions could benefit TWC aftertreatments. Therefore, G-DI vehicle had the lower NO_x emissions of the RDE test in the motorway section. In contrast, the HEV vehicle exhibited an opposite trend to the G-DI and diesel vehicles, with air-fuel ratios in the following order: urban < rural < motorway. This aspect, at least from the air-fuel control perspective, promotes better NO_x conversion, specifically for urban areas. However, the G-HEV engine tended to operate in enriched conditions (with $\lambda < 1$) during 82 and 66 % of the working time in the warming-up and RDE routes, respectively. HEVs tend to a fuel-economy strategy; therefore, the ICE restarts at high-efficiency stages, which means high engine speed, power, and air-fuel ratios. This leads to the relative decrease in engine-out NO_x emissions and better conditions for the NO_x reduction by the TWC. However, the enriched in-cylinder combustion causes insufficiency of oxygen, which leads to higher HC and CO emissions. This was explained by the high HC and CO engine-out emissions, poor performance of the TWC during warming-up, and limited conversion of these pollutants under rich conditions in (Gao et al., 2019a). In addition, high particle number (PN) than ICE-only vehicles were reported by (Yang et al., 2019), and not benefit in the case of unregulated emissions (Suarez-Bertoa and Astorga, 2016). In a novel study with convoy-type RDE tests that compared full hybrid and conventional models, (Huang et al., 2019) reported that HEVs had a fuel reduction of 23–49 %, but the hybrid vehicles exhibited no reduction in HC emissions and consistently higher CO emissions in comparison with

the same conventional vehicles. This was attributed to the frequent stops and starts, lowered exhaust gas temperature, and diminished TWC effectiveness. The results of the present study also demonstrate the importance of air-fuel ratio values.

4.6. Aftertreatment systems performance and tailpipe exhaust gas temperatures

The comparison of tailpipe exhaust gas temperatures shows the general expected temperature levels for all vehicles (**Figure 4.5a**), ordered as motorway > rural > urban $\geq$ hot running > cold start. The figure reflects the direct relation of exhaust temperatures to the power demand, which exhibited the same pattern for each section in **Figure 4.1**. The values and trends were similar between fuel types, which means that in general terms, the vehicles can be compared. This was important because each vehicle had a different exhaust layout, and the measured temperatures were only a proxy of the aftertreatment temperature.

The gasoline vehicles exhibited higher (median) and broader (interquartile range, IQR) temperature ranges than the diesel vehicles (**Figure 4.5a**). Higher in-cylinder temperatures in SI engines imply higher exhaust gas temperatures. In these engines, the combustion mixture close to slightly lean combustion, and high in-cylinder temperatures lead to higher engine-out NO_x concentrations. Hence, generally, the lower tailpipe NO_x emission levels of gasoline vehicles are primarily due to the high efficiency of the aftertreatment systems. For example, in the on-road study of (Zheng et al., 2018), gasoline vehicles with deactivated TWCs had average NO_x emissions as high as $2300 \pm 600 \text{ mg km}^{-1}$ while vehicles with functional TWCs had $30 \pm 20 \text{ mg km}^{-1}$.

The vehicles with continuous catalysts (TWC and SCR) exhibited similar temperature levels between their urban and hot running sections, which could occur to attain the operating temperatures of catalysts during warming-up. This was reflected in the richer air-fuel ratios values of those vehicles in cold start (**Figure 4.4**). However, the hybrid vehicle exhibited the lowest urban-RDE exhaust gas temperatures in comparison with the other sections and other vehicles. Their urban-RDE temperatures were comparable to the cold start values (**Figure 4.4a**). These low values could be primarily attributed to additional time with the combustion engine turned off by the hybrid system, with convective heat transfer from the exhaust gas to the TWC being cut out. This behaviour was different from those observed in the other vehicles because of the unheated TWC, leading to an additional effect of cooling of the exhaust gas. In the urban driving and during cold start, frequent stops, restarts, low exhaust gas flow, and low load conditions affected the performance of catalytic converters. (Huang et al., 2019) reported higher CO, HC and NO emissions of full hybrid vehicles compared with their conventional counterparts in urban sections.

Figure 4.5. Comparison of NO_x emissions and tailpipe exhaust gas temperatures for each vehicle and test, engine-off periods were not considered (a) comparison of exhaust gas temperatures. Middle bar = median; box height = interquartile range (IQR), IQR = third quartile – first quartile; whiskers = ± 1.5 IQR. (b) distance-specific emission factors and average exhaust gas temperature. Solid lines connect CS with HR sections; dashed lines connect urban and motorway RDE sections. The rural section was not plotted for clarity.

Figure 4.5b compares the average NO_x emission factors with the average temperatures of exhaust gases at the tailpipe. Because engine-out NO_x is correlated with power demand, a higher engine-out NO_x was expected during the motorway than during urban driving. For example, the worse-NO_x-reducers diesel vehicles of this study (D-LNT and D-EGR) showed higher tailpipe NO_x emissions during the motorway section compared with urban and warming-up sections although distance-specific emission factors tend to decrease motorway emission factors by higher speeds. The influence of exhaust gas temperatures implied that the D-SCR vehicle was more effective in controlling NO_x emissions in the motorway sections than in the urban ones. The SCR vehicle had urban NO_x emission factors 3.3 times that of the motorway section. In urban conditions, its emissions were 1.6 times the Euro 6 limit, while it was only 0.6 times the limit in the motorway section. Considering the importance of urban NO_x emissions on air quality and human health, the thermal management of SCR's monolith requires attention in post-Euro-6b vehicles. In another article, (Mera et al., 2019b) analysed the same SCR vehicle and demonstrated that a large amount of highest instantaneous NO_x emission peaks were produced in the urban section. This was explained by the cooling of the SCR system during motoring and low load and a high acceleration thereafter.

Figure 4.5b shows that the SCR-equipped vehicle outperformed the NO_x reduction of the other ones, but not at the cold start (circular dots), exhibiting similar levels to the other diesel vehicles. Additionally, emissions in urban sections of the D-SCR vehicle were higher than for rural and motorway sections, which highlighted the influence of low exhaust temperatures on the performance of the tested vehicle. For gasoline vehicles, **Figure 4.5b** shows that the full-hybrid vehicle outperformed the NO_x reduction of the direct-injection vehicle, both with TWC, excepting for the cold start with similar emission levels; however, in the other sections, the vehicles reflected opposite patterns. This can

be explained by the different powertrains and injection approaches and the influence of the air-fuel ratio, which are discussed in the preceding sections.

Different methods focused on the cold start and warming up efficiencies of an engine were analysed by (Roberts et al., 2014). A complete analysis of methods to improve thermal management of catalyst was conducted by (Gao et al., 2019b). This study reported reductions in light-off times of 20–90 % with a consequent increment in the efficiency of emissions reduction. However, the study concluded that the best option would be a trade-off between catalyst efficiency, fuel and energy consumption, and avoiding thermal sintering. Additionally, the controllability of the operating temperature becomes important, e.g. with electrical heating, for the numerous engine-off periods of HEV vehicles and the requirement to attain the maximum efficiency in SCR aftertreatments.

The present study was conducted using one vehicle per type of aftertreatment and powertrain. As significant differences were reported in emission evaluations of other studies, a representative sample of the fleet could corroborate the results of the present study. Finally, the tests in this study were performed at warm ambient temperatures. Recent studies indicated the strong negative dependence of ambient temperature and NO_x emissions of Euro 6 vehicles (Grange et al., 2019; Ko et al., 2017; Suarez-Bertoa and Astorga, 2018). Therefore, high NO_x emissions are expected in colder weather situations than in the tested conditions. Higher NO_x emissions of diesel vehicles at lower ambient temperatures are attributed primarily to the LNT and SCR systems working below optimal operation temperatures and the decrease or stopping of the EGR operation to prevent damage to the DPF, EGR cooler and valve (Kwon et al., 2017).

4.7. Chapter conclusions

The main findings of this chapter lead to the following conclusions:

According to the type of fuel, the full HEV vehicle (equipped with an unheated TWC and indirect injection) and the SCR-equipped diesel vehicle had the lowest real-world NO_x emissions in the RDE tests, exhibiting their potential to comply with real-world Euro 6 limits. Conversely, the G-HEV and D-SCR vehicles had the worst performance during the cold start ($t \leq 300$ s), resulting in 1.1 and 2.7 times the Euro 6 NO_x emission limits, respectively. These high cold start emissions were due to improper operating temperatures of the aftertreatment systems. TWC and SCR systems, both continuous catalytic converters, require a minimum operating temperature to light-off, which is conducive to their optimal performance.

The fast decrease in NO_x emissions of the D-SCR and G-HEV vehicles after the cold start was remarkable. The cold start emissions decreased by 92 and 66 % in hot running ($300 < t \leq 600$ s) for the D-SCR and G-HEV vehicles, respectively. Under cold start period, richer air-fuel ratios than urban and hot running sections were observed, this would provide a fast heating up of engine and aftertreatments. Higher exhaust temperatures of

gasoline engines and lower thermal inertias of gasoline exhaust systems could lead to the decreased light-off times of the TWC.

Because engine-out NO_x is correlated with power demand, in principle, higher engine-out NO_x emissions are expected in motorway sections compared with urban sections. However, tailpipe emissions primarily depend on NO_x control systems and their operating conditions. For diesel tested vehicles, the SCR-equipped vehicle outperformed the NO_x reduction of the other diesel vehicles with LNT and only-EGR, but not for the cold start scenario, exhibiting similar emission levels. Also, urban emissions of D-SCR resulted higher than rural and motorway sections, because of low exhaust gas temperatures. The emission factors were 1.6, 0.9, and 0.5 times Euro 6 limit for urban, rural, and motorway sections. This highlighted the influence of low exhaust temperatures on the performance of the tested vehicle for urban air quality.

For gasoline vehicles, both with TWC, the full-hybrid vehicle outperformed the NO_x reduction of the direct-injection vehicle. Except at cold start, the G-HEV exhibited significantly low NO_x emissions of 2.2 and 1.5 mg NO_x km⁻¹ in the total RDE and urban section, respectively. Surprisingly, the G-DI vehicles had high emission levels; this has not been frequently reported for GDI vehicles. The G-DI had emission factors of 300.0 and 295.4 mg NO_x km⁻¹ in the total RDE and urban section, respectively. At the cold start, both vehicles exhibited equivalent emission levels. However, in the other sections, the vehicles reflected emissions with an opposite pattern. This could be explained by the fact that different powertrains and injection approaches were used. While the direct injection engine tended to operate in lean-burn conditions, the PFI engine of the HEV tended to operate in rich conditions. Because NO_x reduction in TWCs is favoured in rich or stoichiometric conditions, the recurrent leaner air-fuel ratios of the G-DI vehicle reduced the efficiency of its TWC aftertreatment. In terms of the powertrain, the HEV tends to a fuel economy strategy; therefore, the ICE operated at high power, which led to the rich air-fuel ratios with the relative reduction in engine-out NO_x emissions and better conditions to the NO_x reduction for the TWC. In addition, the continuous restarting of the ICE could lead to the cooling of the TWC, affecting environmental performance. Under those conditions, high levels of CO, HC, particulate matter and unregulated emissions could be released, as has been reported in other studies on hybrid vehicles. The HEV combustion engine operated much longer in the motorway (99 %) section compared with the urban-RDE (28 %) section. In all the urban sections, the electric mode recurred approximately 50 % of the time. Similar exhaust gas temperatures were observed between G-DI and G-HEV vehicles. However, in urban-RDE sections, the hybrid vehicle had the lowest temperature level in this study, comparable to cold start levels.

The gasoline vehicle with direct injection and the diesel vehicles with EGR-only and LNT aftertreatment did not satisfy Euro 6 limits. To satisfy real-world pollution limits, this gasoline direct injection vehicles would require (a) diesel-like aftertreatment systems, or (b) to meet stoichiometric combustion in all driving conditions. The results suggest that diesel vehicles require SCR systems to satisfy real-world emission limits. Finally, the SCR-diesel and HEV vehicles can improve the aftertreatment thermal management to

further exploit their potential for pollution reduction. Therefore, to comply with post-Euro-6 regulations, these vehicles should be equipped with active heaters for the aftertreatment devices, with an optimal trade-off between pollution reduction and fuel-economy penalty.

CHAPTER 5

Investigations of the high NO_x emissions from diesel passenger cars*

The high emission sets (see Section 3.3.1.5) HES-20, HES-50 and HES-80 that corresponds to the 20, 50 and 80 % of total emissions of each vehicle were used to evaluate the impact of high NO_x emissions on the emission factors. The analysis was performed with diesel vehicles and tests carried out in Madrid.

For this purpose, the events of high instantaneous NO_x emissions (emission peaks) were clustered. Then, their contributions to emission factors and their weighting in driving time were assessed. Finally, they were characterized with respect to the following EOVs and IOVs parameters: vehicle speed, positive acceleration (a^+), speed times positive acceleration ($v \cdot a^+$), relative air-fuel ratio (λ) and exhaust gas temperature at the tailpipe, and road grade.

The performance and type of NO_x control technology installed in the vehicle is a determinant factor that influences the release of NO_x emissions. Therefore, all the stages of this study also assessed the differences between the tested vehicles. The three SUV diesel passenger cars D-SCR, D-LNT, and D-EGR, were selected to analyse in detail the instantaneous NO_x emissions. All the vehicles are diesel-fuelled; therefore, in this chapter, the vehicles' ID is simplified to SCR, LNT, and EGR, respectively. The analysed vehicles had the following common characteristics: common rail direct injection, variable geometry turbocharger (VGT), 6-speed manual gearbox and stop-start system. Also, standard commercial diesel fuel was used for all tests. The characteristics of the vehicles are shown in **Table 3.2**.

Only hot-start valid RDE valid tests were analysed, and cold start emissions data was not used. Each vehicle performed five RDE tests, see **Table 3.2**, but only ten tests resulted valid, it represented EGR (3), LNT (4) and SCR (3). Four tests were excluded for exceeding moderate ambient temperature conditions. Another test was discarded for exceeding ($v \cdot a_{pos}$) [95] limit in the verification of the overall trip dynamics. The dataset of all valid RDE tests for each vehicle i , is defined as RDE-S _{i} (RDE Set) in this chapter. RDE-S data summed 765 km, and total testing time of 16 hours and 50 minutes, resulting in ~600 thousand observations.

Figure 5.1 shows that high NO_x emissions are short events that occur throughout the trip. Therefore, cumulated emissions are mainly represented by these short-time events. For each vehicle, this figure contains raw instantaneous NO_x emissions for an RDE test

* Main source (Mera et al., 2019b)

with the maximum emission peak of NO_x . It also represents vehicle speed and the values of NO_x thresholds (h_L) for each high emission set. For example, the LNT vehicle had the event of maximum NO_x emission between ~ 4700 and ~ 4710 seconds. This peak surpasses the three NO_x thresholds, so observations of this event belong to the three high emissions sets: HES-20, HES-50 and HES-80. Previous studies noted that high emissions correspond to emission peaks, which are usually smoothed or treated as outliers. These high emissions also increase the emission factors, mainly in conditions of high dynamics (Heijne et al., 2016; O'Driscoll et al., 2016). In **Figure 5.1**, the maximum peaks of EGR and LNT vehicles match with strong acceleration at high speeds. However, the emission peaks and HES threshold are significantly reduced by the vehicle equipped with the SCR system.

Figure 5.1. Raw PEMS data of instantaneous NO_x emissions and vehicle speed. Horizontal dashed lines show the different thresholds (h_L) of each vehicle and each high emission set.

5.1. Impact of high instantaneous NO_x emissions on driving time

Figure 5.2 shows the high emissions sets: HES-20, HES-50 and HES-80 for each vehicle. Every HES-L is characterized in the figure by the percentage of cumulated NO_x (dot-dashed vertical lines). Every line intersects with three instantaneous NO_x emissions (black lines) values, which represent the NO_x threshold for each vehicle. Similarly, every vertical line intersects with the percentage of time (blue lines) values. **Table 5.1.** includes a summary of the numerical results.

An interesting finding is that observations with high instantaneous NO_x emissions, represented by HES, account for a large amount of cumulated emissions in a small percentage of time (or percentage of observations). For example, 80 % of the total emissions (HES-80) were cumulated in approximately 20 % of the total time, namely, 16.2, 22.3 and 16.7 % for EGR, LNT and SCR vehicles, respectively. The remaining 20 % of the total emissions (LES-20) were generated in ~ 80 % of the total time. (Chong et al., 2018) determined that 40 % of the total NO_x emitted during the entire driving test occurred in 7.3 % of the total driving time.

Figure 5.2. High emissions sets (HES) with corresponding low emissions sets (LES) for RDE tests data of each vehicle (RDE-Si). Curves represent NO_x instantaneous emissions (black) and percentage of time (blue).

SCR vehicle reduced instantaneous NO_x emissions in the entire range of possible emission values. In **Figure 5.2**, the instantaneous emissions (black) and time (blue) curves of HES have similar profiles for the three tested vehicles, but the EGR instantaneous emissions are not only higher than that of LNT but also much higher than that of SCR emissions. Therefore, HES threshold values of instantaneous NO_x have the same tendency, as shown in **Table 5.1**.

The upper limit of the time percentage curves (blue in **Figure 5.2**) shows that there were no NO_x emissions during a substantial amount of time: 12 % (EGR), 13 % (LNT) and 21 % (SCR). This corresponds to the stop periods ($v < 1 \text{ km h}^{-1}$). RDE tests resulted in average stop periods of 16.6 % (EGR), 18.4 % (LNT) and 17.7 % (SCR). Under these conditions, unless the engine is turned off by the stop-start system, there is a low NO_x concentration and a low exhaust gas flow.

Table 5.1. NO_x thresholds and percentage of time of high emissions sets (HES)

High emissions set	Cumulated NO _x [%]	EGR		LNT		SCR	
		NO _x threshold	Time	NO _x threshold	Time	NO _x threshold	Time
		[mg s ⁻¹]	[%]	[mg s ⁻¹]	[%]	[mg s ⁻¹]	[%]
HES-20	20	88.8	1.5	66.2	1.6	21.3	0.7
HES-50	50	44.2	5.9	25.6	7.3	6.5	3.7
HES-80	80	15.4	16.2	8.7	22.3	1.3	16.7

5.2. Impact of high instantaneous NO_x emissions on emission factors

To assess the impact of high NO_x on emission factors, NO_x thresholds (hL) were used as maximum values of RDE tests. Thus, the observations that belong to HES were replaced by their respective NO_x threshold. Then, emission factors were recalculated and compared to the emission factors of actual RDE tests.

In addition to the computation of the raw distance-specific emission factor, for the entire RDE tests, weighted distance-specific emission factor (EF_w) was computed. It establishes fixed distance proportions for each RDE section:

$$EF_w = 0.34 \cdot EF_u + 0.33 \cdot EF_r + 0.33 \cdot EF_m \quad (5.1)$$

where the emission factors for the sections of the RDE test are represented by the sub-indexes u , r , and m . The weightings for the RDE test sections of Reg. (EU) 2017/1151 regulation correspond to proportions of 34 % (urban), 33 % (rural) and 33 % (motorway), respectively. In addition, the dimensionless term emission factor ratio ($EF\phi$) was also implemented to compute the mean contribution of each section to the weighted emission factor.

$$EF\phi = \frac{EF_k}{EF_w} \quad (5.2)$$

where EF_k is the emission factor for a given section k and EF_w is the weighted emission factor. **Figure 5.3** shows the actual weighted emission factors as white bars. EGR and LNT vehicles had the highest emission factors for any section or test ($DR_k = 5.1\text{--}13.0$). Therefore, they significantly exceeded the Euro 6 type-approval limit for diesel passenger cars ($80 \text{ mg NO}_x \text{ km}^{-1}$) and NTE Euro 6d-TEMP limit ($210 \text{ mg NO}_x \text{ km}^{-1}$). On the other hand, the emission factors of the SCR vehicle are under the NTE limit and sometimes under the Euro 6 limit, with $DR_k = 0.6\text{--}1.6$. The results in (Yang et al., 2015a) showed that vehicles with these three NO_x control technologies complied with Euro 6 limits in the NEDC cycle, however, they did not in the WLTC cycle. In the case of the WLTC cycle, vehicles with SCR presented fewer NO_x emissions factors compared to the vehicles with EGR-only and LNT systems. In other studies with PEMS, (May et al., 2014; Triantafyllopoulos et al., 2018; Weiss et al., 2012) have also shown that SCR systems have the potential to reduce NO_x emissions. The extensive research of (O'Driscoll et al., 2016) found that SCR and LNT technologies were able to meet the Euro 6 standard, but EGR alone was not. Recent studies show that the EGR system could improve the trade-off between NO_x emissions and fuel consumption in diesel engines by the use of asymmetric twin-scroll turbocharging (Zhu and Zheng, 2017), and improve even more its performance using two EGR circuits (Zhu and Zheng, 2019). Nonetheless, these results and the current stringent legislation emphasizes the need to use SCR systems to satisfy Euro 6 and futures emission limits in real-world driving conditions.

Figure 5.3. Comparison of tested and reduced emission factors. Weighted and raw distance-specific emission factors from tests (white bars). In greyscale, the reduced emission factors based on the NO_x thresholds as maximum values of instantaneous NO_x emissions. The bars below the horizontal axis represents the reduction percentage of emission factors of the upper bars. The error segments represent ± 1 sd. NTE limit corresponds to 168 mg NO_x km⁻¹ of Euro 6d-Temp (CF = 2.1)

The SCR tested vehicle is efficient at reducing NO_x emissions, particularly in the motorway section. Similar trends for the comparison of SCR vehicles in urban and motorway sections were found in (O'Driscoll et al., 2016). Although the SCR vehicle had low emission factors, its emission factor ratios show that urban section ($EF_u = 1.40$) had a much greater contribution compared to the motorway section ($EF_m = 0.50$), as highlighted in **Table 5.2**. This resulted in emission factors in the following order: $EF_u > EF_w > EF_m$, with average DR values for urban (1.6), weighted (1.1) and motorway (0.6), as the lowest emission factor in the study. However, for EGR and LNT vehicles, their emission factor ratios show that rural and motorway ($EF_r = 0.93$ – 1.50) contributed more than urban ($EF_u = 0.58$ – 0.85). Their motorway emission factors were similar to the weighted emission factors and greater than the urban emission factors, namely $EF_m \approx EF_w > EF_u$. Thus, worse-NO_x-reducers (EGR and LNT) vehicles had average deviation ratios for motorway (8.0, 7.7), weighted (8.7, 7.4) and urban (5.1, 6.3). At the tailpipe, the measured emissions are related to the overall environmental performance of the vehicle. However, from the perspective of the engine, tailpipe emissions are related to NO_x control system performance, and vehicles were defined as better or worse NO_x-reducer.

Table 5.2. NO_x emission factors ratio (EF_φ)

EF _φ	EGR	LNT	SCR
EF _u / EF _w	0.58	0.85	1.40
EF _r / EF _w	1.50	1.11	1.08
EF _m / EF _w	0.93	1.05	0.50

Grey cells are sections where emissions are less than the weighted emission factors.

Figure 5.3 also shows the reduced emission factors by the NO_x thresholds and the correspondent percentage of reduction. It should be noted that observations with emission peaks were not removed, but they were constrained to their threshold value to determine the impacts of high NO_x on the emission factors, as is explained at the beginning of this chapter. Depending on HES set, weighted emission factors were reduced by 30–38 % for HES-20, 54–58 % for HES-50, and 79–82 % for HES-80. It shows the big impact of the highest emissions, e.g. HES-20, which represents only 20 % of the total emissions in a small percentage of driving time (0.7–1.5 %).

Comparing RDE sections, worse-NO_x-reducers (EGR and LNT) vehicles had a greater impact on rural (reduction of 37–85 %) and motorway sections (reduction of 42–88 %). SCR exhibited a similar reduction percentage for the rural section (47–87 %). The lowest impact was always on the urban section for the three vehicles; however, the SCR vehicle showed higher percentages of reduction than the others, with a reduction of up to 80 %. To accomplish with normative, Euro 6 limits must be achieved in urban and entire RDE tests. Therefore, SCR vehicles could satisfy Euro 6 limit by reducing NO_x emissions of HES-50, which would result in DR_u = 0.9 and DR_w = 0.8. However, EGR and LNT vehicles could almost satisfy the NTE limit by reducing HES-80, both with DR_u = 2.2, and DR_w of 1.5 and 1.9, respectively.

These results imply that NO_x emission factors could be substantially reduced if NO_x emission control and aftertreatment systems are effectively applied to these emission peaks. Therefore, it is relevant to investigate the conditions where these high emission events occur, so this study also performed an analysis of HES with respect to other parameters. The findings are discussed in the following sections.

5.3. Analysis of driving and engine operating parameters

A descriptive statistical analysis was performed to find relationships between high instantaneous NO_x emissions and the analysed parameters. Two methods were applied for the analysis. For each parameter, the first method compares the high NO_x emissions (HES) with respect to the total number of observations (frequency distributions of RDE-S_i).

The frequency distributions of HES are affected by RDE testing conditions and occurrence, i.e., HES frequency distributions are likely to be greater in RDE test values with a high occurrence (high frequency). Therefore, the second method used conditional probabilities, represented by the proportion of the number of observations for high NO_x emissions compared to the number of observations of RDE-S_i. In this way, the conditional

distribution illustrates the conditions whereby high NO_x emissions are present, regardless of the test conducted. Strictly speaking, it could be computed using the conditional probability mass function of $X = x$, given $Y = y$, using the equation:

$$g(x|y) = \frac{f(x, y)}{f_Y(y)} \quad (5.3)$$

For any analysed parameter, X and Y are discrete random variables. $X = \{0, 1\}$, where 1 means belonging to HES, and 0 indicates does not belong. $Y = \{a_1, a_2, \dots, a_n\}$, where a is the count of the parameter in each bin of RDE-S_i data (discretized in n bins). In the equation, $f(x, y)$ is the joint probability distribution, and $f_Y(y)$ corresponds to the marginal probability distribution. Thus, plots with conditional probability mass function of $X = 1$, given RDE-S_i data are shown for each analysed parameter.

5.3.1. Vehicle speed

The vehicle speed profiles of the RDE tests were similar, and this allowed them to be compared. For the RDE-S_i of each vehicle, **Figure 5.4** shows similar cumulative and probability density functions of the speed (blue lines). RDE-S_i average speeds were: 45.4 km h⁻¹ for EGR, 44.8 km h⁻¹ for LNT, and 46.3 km h⁻¹ for SCR. **Figure 5.4a** also shows the cumulative density function (merged vehicles) for urban, rural and motorway sections. It is observed that each section has a well-differentiated speed profile. Specifically, speed ranges were between the 5th and 95th percentiles for 0–48 km h⁻¹ for urban and 20–89 km h⁻¹ for rural sections, while speeds over 75 km h⁻¹ (5th percentile) were measured for motorway sections. This resulted in RDE test mode (Mo) values of Mo_{urban} ≈ 44 km h⁻¹, Mo_{rural} ≈ 87 km h⁻¹, and Mo_{motorway} ≈ 121 km h⁻¹, as shown in **Figure 5.4b**.

WLTC and NEDC cycles are also plotted in the figure, and it is observed that the RDE speed profiles were more similar to the WLTC cycle than the NEDC cycle; although the WLTC cycle does not have the same speed mode values as the RDE speed distribution.

Figure 5.4. Vehicle speed distributions for NEDC, WLTC and RDE tests of each vehicle (RDE-S_i) (a) cumulative density function (b) probability density function

For the three tested vehicles, **Figure 5.5a** compares RDE tests (RDE-S_i) frequency distributions (the grey area) and frequency distribution of the high emissions sets previously defined: HES-80, HES-50 and HES-20. Frequency distribution curves have been normalized to facilitate an easier comparison. As a result, **Figure 5.5a** shows that

high instantaneous NO_x emissions were mainly generated in the modal speed values of each RDE section (urban, rural and motorway). Surprisingly, these modes occurred at speeds that were close to the speed limits of urban and motorway sections. Speed limits are a very important factor in driver's speed selection, and there is a tendency for the coordination of speed between drivers to maintain a uniform running speed (Elvik, 2014, 2010). Therefore, high NO_x emissions in real-world driving or in RDE tests will occur with a high frequency at speed values related to traffic regulations and/or design of the RDE route. Although the speed limits of the tested RDE route (in Madrid, Spain) were 50 km h^{-1} for urban and 120 km h^{-1} for highway, RDE regulation in (EC, 2017) established speed limits of 60 km h^{-1} for urban and 145 km h^{-1} for motorway driving.

Figure 5.5. Vehicle speed distributions (a) frequency distribution values of high emission sets (HES) on the left axes, and RDE tests (RDE-S_i) on the right axes. Frequency distributions are normalized, RDE-S_i = 1000 observations (b) conditional probability distribution of HES

Figure 5.5b shows the probability of producing high NO_x emissions regardless of the RDE tests frequency distribution. EGR and LNT vehicles were more likely to emit high instantaneous NO_x at high speed. These vehicles increase the conditional probability of high emissions as speed increases so that their curves show a negative asymmetry. In **Figure 5.5a**, EGR and LNT vehicles have a higher frequency of HES observations in high-speed modes (rural and motorway) than the low-speed mode (urban), although the opposite pattern for RDE distribution is evident. According to (Myung et al., 2017; Weiss et al., 2011b), these NO_x control technologies reduce performance during high-engine-load driving due to: limitation of gas recirculation in EGR and limitation of storage capacity in LNT systems.

Compared with EGR and LNT vehicles, the SCR vehicle showed different patterns of frequency and conditional distributions for HES observations (**Figure 5.5a**). The SCR vehicle exhibits a higher frequency of HES observations for urban and rural modes, with a considerable reduction in the frequency of motorway speed mode. The highest NO_x peaks (HES-20 and HES-50) for speeds above 110 km h⁻¹ are not present, while **Figure 5.5b** shows a slight increase of the HES-80 probability at low speeds (approximately 25 km h⁻¹). The patterns of the SCR vehicle agree with the effective reduction of emission factors exhibited by this vehicle, specifically in the motorway section. According to (Yang et al., 2015b), on average, the SCR system performs better than EGR-only and LNT systems in high-speed ranges. This was also evidenced in extra-high-speed sub-cycles of WLTC in (Yang et al., 2015a)

5.3.2. Positive acceleration (a^+) and speed times positive acceleration ($v \cdot a^+$)

Figure 5.6 shows cumulative density functions (CDF) for positive acceleration (a^+) and vehicle speed times positive acceleration ($v \cdot a^+$) for RDE tests of each vehicle (RDE-S_i). It is observed that these two functions are similar for all the vehicles (black lines). The motorway section (dotted grey line) had lower records of a^+ and higher records of $v \cdot a^+$ compared to the other RDE sections. Conversely, the urban section (continuous grey line) showed an opposite pattern to the motorway section.

Real-world driving tests had $v \cdot a^+$ values over the maximum values of NEDC and WLTC cycles, particularly in rural and motorway sections. The dot-dashed red line ($v \cdot a^+ = 9.2 \text{ m}^2 \text{ s}^{-3}$) represents the maximum value of $v \cdot a^+$ in the NEDC cycle, in addition to the threshold between “mild” and “strong” driving severity according to (Franco et al., 2014). Similarly, the dot-dashed blue line ($v \cdot a^+ = 20.1 \text{ m}^2 \text{ s}^{-3}$) represents the maximum value of $v \cdot a^+$ in the WLTC class 3b cycle. Thus, in **Figure 5.6b**, it is observed that 15–18 % of the acceleration time for the entire RDE tests coincided with “strong” driving. This corresponds to 31–34 % of the acceleration time of the motorway, 25–27 % of rural, and 4–7 % of urban sections. It is also observed that only 2–3 % of the RDE total acceleration time had $v \cdot a^+$ values above the threshold of the WLTC cycle.

Figure 5.6. Cumulative density functions of RDE tests of each vehicle (RDE-S_i) (a) positive acceleration (a^+) (b) vehicle speed times positive acceleration ($v \cdot a^+$), and maximum values for NEDC and WLTC cycles

Figure 5.7 show a^+ and $v \cdot a^+$ boxplots for high NO_x emissions sets (HES-20, HES-50 and HES-80) and RDE- Si . High emissions have a positive correlation with high $v \cdot a^+$ values for all vehicles. In the case of EGR and LNT vehicles, these $v \cdot a^+$ values are related to a strong acceleration at elevated speeds. This is clearly illustrated in the emission peaks of the raw data (**Figure 5.1**), considering that the emission factors and HES speed observations were relevant in rural and motorway sections for EGR and LNT vehicles. As stated by (Heijne et al., 2016), higher speeds and higher dynamics increases NO_x emissions in diesel Euro 6 vehicles. It was also stated by (Costagliola et al., 2018) about high instantaneous emissions of two Euro 5 EGR-only diesel vehicles. In (Chong et al., 2018) high NO_x emissions of Euro 6 LNT diesel vehicles are attributed to high speed, high acceleration, low EGR mass flow rate, and regeneration of the diesel particle filter (DPF).

Figure 5.7. Boxplots for high emissions sets (HES) and RDE tests (RDE- Si) (a) positive acceleration (a^+) (b) vehicle speed times positive acceleration ($v \cdot a^+$). The dot-dashed lines indicate the maximum $v \cdot a^+$ values of NEDC and WLTC cycles. The central line in boxplot = median, green rhombus = mean.

Even though the SCR vehicle reduced emissions (especially on the motorway), its relatively high emissions were produced mostly in the urban and rural sections. With changing speeds, these sections usually reflect high a^+ values. In **Figure 5.7a**, the SCR vehicle shows a positive correlation of high NO_x emissions with a^+ (it is less evident for the EGR and LNT vehicles). This is consistent with the observations of (O'Driscoll et al., 2016) who noted high NO_x emissions in sub-trips with high RPA at low speeds.

Figure 5.8. $v \cdot a^+$ conditional probability for high emission sets (HES) on the left axes. On the right axes, the grey area represents $v \cdot a^+$ frequency distribution of RDE tests (RDE- Si); normalized as RDE- Si = 1000 observations. The dashed lines indicate the maximum $v \cdot a^+$ values of NEDC and WLTC cycles.

For $v \cdot a^+$, **Figure 5.8** shows the probability of HES observations independent of the RDE-S_i frequency distribution. It is observed that the three vehicles have higher conditional probabilities for high NO_x emissions as $v \cdot a^+$ increases, although the RDE-S_i frequencies are left-shifted. The conditional probability is more relevant when $v \cdot a^+$ is higher than the “strong” driving conditions of NEDC, and this probability is much larger when $v \cdot a^+$ surpasses the maximum value of the WLTC cycle. For example, “strong” $v \cdot a^+$ values had minimum conditional probability for HES-80 emissions of 45 %, 62 % and 34 % for EGR, LNT and SCR vehicles, while $v \cdot a^+$ values over maximum $v \cdot a^+$ value of WLTC (blue line) had at least 90 %, 93 % and 70 % probability of being HES-80 emissions, respectively.

Therefore, it is verified that parameter $v \cdot a^+$ is a robust indicator for the assessment and prediction of high instantaneous NO_x emissions for the three NO_x control technologies. This hypothesis could be assessed in a wide-ranging vehicle fleet.

5.3.3. Relative air-fuel ratio (λ) and exhaust gas temperature

The thermal NO_x formation is described by the Zeldovich mechanism (Zeldovich et al., 1947). Under these conditions, the flame temperature is high, and there is excess oxygen during the flame diffusion process in diesel engines (Guardiola et al., 2017; Reşitoğlu et al., 2015). Therefore, it is usual for diesel engines to generate more NO_x in the motorway and rural sections because higher engine loads are required (Carslaw et al., 2013b; Gallus et al., 2017). Under these conditions, an increase in fuel injection and a reduction of the relative air-fuel ratio occurs. (Guardiola et al., 2017; Heywood, 1988). All the tested vehicles had stop-start systems; therefore, the relative air-fuel ratio and exhaust gas temperature were not analysed during engine-off periods (engine speed < 50 rpm).

The relative air-fuel ratio was measured at the tailpipe. Box plots for HES and RDE tests are shown in **Figure 5.9**. Similar to the results from Section 4.5 and 4.6, it was determined that most of the high instantaneous NO_x emissions occurred under slightly lean-mixture burn conditions ($1 \lesssim \lambda \lesssim 1.5$) as measured at the tailpipe. As shown in this figure, the HES of three tested vehicles had at least 75 % of their lowest observations (75th percentile) for HES-20 and HES-50 within that range, and at least 50 % of the lowest observations (median) for HES-80 also in this range. In comparison, RDE-S_i boxplots revealed that more than 75 % of the observations with the highest values exceeded that range ($\lambda > 1.5$). The engines of the tested vehicles frequently operated with a slightly lean mixture ($1 \lesssim \lambda \lesssim 1.5$) in the rural and motorway sections due to the higher power demand. These sections were within that range approximately 30–35 % of the time, while the urban section had only 10 % of the time under this condition. These results are consistent with the expectations upstream of the aftertreatment systems and in combination with the other measured parameters, could form robust predictors for the identification of high instantaneous NO_x emissions.

Figure 5.9. Boxplot comparison of tailpipe relative air-fuel ratio (λ) for High emissions sets (HES) and RDE tests (RDE-S_i); central line in boxplot = median, green rhombus = mean, the y-axis is trimmed at the top to improve visualization.

The cumulative density functions of the tailpipe exhaust gas temperature are shown in **Figure 5.10**. It is observed that the exhaust gas temperature of the three tested vehicles (black line) had similar profiles. Clearly, the temperatures for the motorway section (average 133–151 °C) are greater than that of the urban section (average 69–82 °C).

Figure 5.10. Tailpipe exhaust gas temperature cumulative functions of high emissions sets (HES), RDE tests (RDE-S_i), urban and motorway sections.

Figure 5.10 also shows that the CDF curves of HES-20, HES-50 and HES-80 have higher temperature values than RDE-S_i distributions. The tested vehicles showed different association patterns between high NO_x emissions and exhaust gas temperatures. Worse-NO_x-reducers (EGR and LNT) vehicles had most HES observations related to “high” exhaust gas temperatures (≥ 75 °C). EGR-only vehicle exhibited homogeneous behaviour

and had similar curves between different HES sets, with values ranging from ~ 75 °C to 212 °C and average 134.5 (sd. 12.6) °C

Exhaust gas temperature and engine load values constrain the performance of exhaust gas aftertreatment systems. For the LNT vehicle, the highest emissions (HES-20) temperatures approximately corresponded to the rural and motorway sections, where engine load is high, thereby overgrowing LNT storage capacity. In this study, SCR exhibited high effectiveness in rural and motorway sections. **Figure 5.10** also shows that the SCR vehicle mainly reduced NO_x emissions for tailpipe exhaust gas temperatures of approximately 80–190 °C. Therefore, a low slope curve was observed for HES in this range. Observations above 190 °C show high NO_x emissions. This could be because SCR aftertreatment has an optimum internal operating temperature of approximately 300–400 °C (Yang et al., 2015a), and it also requires an activation threshold temperature of ~ 200 °C (Ntziachristos et al., 2016). SCR had relatively high urban emission factors. Depending on the HES set, it is observed that between 20–60 % of high instantaneous emissions occurred at “low” exhaust gas temperatures (< 80 °C). In addition, aftertreatment can be affected by high-temperature exhaust gas during the regeneration process of the DPF, so thermal management of aftertreatment systems is an important research area.

Figure 5.11. Conditional probability of tailpipe exhaust gas temperature for high emission sets (HES) on the left axes. On the right axes, the grey area represents the frequency distribution of RDE tests (RDE-S_i); normalized as RDE-S_i = 1000 observations

Although the exhaust gas temperatures of the RDE tests exhibit a high frequency at approximately 75 °C (grey area), all HES conditional distributions showed negative asymmetry (**Figure 5.11**). This means that HES observations are more likely to appear at increasing exhaust gas temperatures, independent of the RDE test performed. The distributions of EGR and LNT vehicles show upward probabilities of HES observations over “low” exhaust gas temperatures of 75 °C. However, the SCR vehicle substantially increased the probability of high instantaneous emissions for exhaust gas temperatures over 150 °C, due to high load in motorway and probably by DPF regeneration.

5.3.4. Road grade

The RDE route was approximately a closed loop, which means that there were equally positive and negative cumulative gains, as shown in the cumulative distributions of road

grade for RDE tests in **Figure 5.12**. However, 60–80 % of HES observations occurred during uphill (road grade > 0). Therefore, high instantaneous NO_x emissions are more likely to be produced on positive slopes due to higher engine load. (Gallus et al., 2017) also determined that NO_x emissions had a strong linear correlation with road grade, while (Costagliola et al., 2018) found a second-order positive correlation between road grade and NO_x emissions in real-driving of rural sections. In **Figure 5.12**, slopes less than -1.3% had relatively few HES observations for EGR and LNT vehicles due to the fuel cut off and low engine load. The SCR vehicle reduced emissions in the entire range of possible values; therefore, their HES curves show a small difference compared to their RDE-S curve.

Figure 5.12. Road grade cumulative functions of High emissions sets (HES) and RDE tests (RDE-S_i).

Strictly speaking, some of the numerical results of this study are limited to low-mileage vehicles of the same tested models. Literature shows that Euro 6 vehicles have a wide variability of NO_x emission levels; because, NO_x emissions depend on NO_x control technology and its configuration, management, usage time and maintenance (Lee et al., 2019). However, the applied methodology used to classify HES and to analyse them, and the patterns identified in these investigations could be extrapolated to other diesel passenger vehicles at this time.

5.4. Chapter conclusions

The main findings of this chapter lead to the following conclusions:

The instantaneous NO_x emissions of each vehicle were sorted and clustered in high emissions sets (HES). The contribution of these HES to real-world cumulated emissions showed the same patterns for all vehicles, and it led to the same conclusion: HES are composed of few observations with NO_x emission peaks, which means that high instantaneous NO_x emissions represent a large amount of cumulated emissions in a small amount of driving time. Although their theoretical constraint reduces emission factors by 30–82 %, NO_x emissions in the entire range of operation should be reduced to achieve Euro 6 real-world limits.

In relation to RDE tests, high instantaneous NO_x emissions are mainly generated in one modal speed value for each urban, rural and motorway sections. These speed modes

mainly depend on road speed limits or RDE regulation. This suggests that hot spots in these operating conditions could be identified and tackled by NO_x control systems and anti-pollution policies.

The high instantaneous NO_x emissions were mainly produced in slightly lean mixture conditions ($1 \lesssim \lambda \lesssim 1.5$) and high exhaust gas temperature. These conditions that are indicative of high load were more frequent in the motorway section than urban section. For the worse-NO_x-reducers of this study, these results are also explained by the shortcomings of their NO_x control technologies at high loads: limited recirculation of exhaust gas in EGR, and limited storage capacity in LNT systems.

The most frequent value of tailpipe exhaust gas temperatures was 75 °C for all vehicles. For worse-NO_x-reducers (EGR and LNT) vehicles, almost all high instantaneous NO_x emissions were at “high” temperatures (over 75 °C). On the other hand, the SCR vehicle reduced the emission factors, but it had its relatively high emissions in the urban section, with a deviation ratio of 1.6. In this section, the SCR system is affected by low operating temperatures. Low operating temperatures of NO_x control systems can be produced by long stop periods (in traffic situation) and low exhaust gas flow in conditions of low-speed driving and deceleration, which are typical conditions of urban driving and sometimes present in rural sections.

Uphill, where a high engine load is required, showed larger probability to yield high instantaneous NO_x emissions. Between 60–80 % of high instantaneous NO_x occurred uphill (road grade > 0).

Driving severity increases the probability of high NO_x emissions. The driving conditions with strong potential to generate HES observations are $v \cdot a^+ > 9.2 \text{ m}^2 \text{ s}^{-3}$ (NEDC limit). For worse-NO_x-reducers (EGR and LNT) vehicles, the conditions of elevated vehicle speed with hard acceleration (high $v \cdot a^+$) produced high NO_x emissions, particularly in rural and motorway sections. On the other hand, the relatively high NO_x emissions of SCR vehicle were also related to high $v \cdot a^+$ values; however, they matched with conditions of hard acceleration at low vehicle speed, particularly in urban and rural driving. Therefore, $v \cdot a^+$ is a robust indicator to assess and predict high instantaneous NO_x emissions. As such, speed reduction policies can lead to NO_x emissions reduction if they do not increase driving dynamics; namely, allowing fluid traffic with constant speed and limiting stops or hard accelerations. In addition, since $v \cdot a$ is the main parameter in VSP, this corroborates the use of VSP as a good explanatory variable for NO_x emission models.

High instantaneous NO_x emissions are produced in short time periods and are dependent on in-cylinder and aftertreatment operation; therefore, they are harder to identify and control. The methodology presented in this study identifies the conditions and probabilities required to find them so that this information could improve micro and meso emission models, which are based on data from the engine and/or vehicle operating conditions. It could also help to predict the action of SCR systems.

CHAPTER 6

SCR efficiency during warm conditions

In the past chapters, the NO_x emission peaks were analysed and characterised based on using (a) EOVs such as speed, acceleration, $v \cdot a$, road grade, and VSP, and (b) IOVs such as air-fuel ratio and exhaust gas temperatures. Given the importance of NO_x peaks on total emissions and microscopic emission models, this chapter analyses in depth the NO_x emission released from more detailed data. The data was measured in real-world tests for an SCR-diesel passenger car by TUGraz.

6.1. Distance-specific emission factors

Figure 6.1 shows the distance-specific tailpipe emission factors for the regulatory cycles and the two more representative on-road tests. This figure reflects that on-road NO_x emissions were higher than the emissions from the laboratory cycles. The total on-road NO_x emission was 1.5–2.1 times the reported type approval (NEDC) value of $58.5 \text{ mg NO}_x \text{ km}^{-1}$. This is usually explained by the different boundary testing conditions between the type approval cycle and the real-world driving (Franco et al., 2013), which at least results in a bias towards the NEDC cycle. On the other side, the on-road emissions were 0.6 times the NTE limit of $168 \text{ mg NO}_x \text{ km}^{-1}$ (with a conformity factor 2.1).

Considering the Euro 6 limit of $80 \text{ mg NO}_x \text{ km}^{-1}$, the average deviation ratios for the entire and urban part of on-road tests were 1.29 and 1.35, respectively. Although the tested vehicle accomplishes its legislative NO_x levels, it reflects the need for improvement in deNO_x conversion to reduce real-world NO_x levels, and it is even outside the current RDE boundary limitations for future more stringent emission regulations.

Figure 6.1. Distance-specific tailpipe emission factors (a) NO_x emissions and deviation ratios, NTE limit is 168 mg km^{-1} (conformity factor 2.1). Error segments = ± 1 standard deviation.

6.2. Highest instantaneous NO_x emissions

In this study, the NO_x threshold was determined for 50 % of cumulative emissions from all RDE tests, following the methodology described in Section 3.3.1.5. Therefore, the threshold h_{50} (mg s⁻¹), represents the minimum emission level from all subset HES-50 observations. This threshold (h_{50}) for the RDE tests, resulted in 14.2 and 2.0 mg s⁻¹ for the entire and urban part, respectively. Surprisingly, the cumulated NO_x emissions of HES-50 only represented 2.6 % and 4.7 % of total and urban driving time. Equivalent results were found for the NO_x emissions peaks from a Euro 6b SCR vehicle tested in Madrid (Mera et al., 2019b), where the HES-50 threshold for the RDE tests resulted in 6.5 mg s⁻¹, and it was emitted during only 4 % of the total driving time. Owing to its impact in the actual emission factors and the low occurrence, HES observations are a key cluster to be analysed in NO_x emission investigations. In this chapter, HES-50 observations were considered for every analysed parameter and plotted in figures, to identify their occurrence conditions since NO_x concentrations and temperatures upstream and downstream of the SCR catalyst are available.

6.3. Instantaneous NO_x emissions during on-road tests

For the entire RDE trip, **Figure 6.2** shows profiles for the engine-out and SCR-inlet exhaust gas temperatures, with two references for low (200 °C) and high temperatures (350 °C). Below these profiles, and for the urban section in **Figure 6.3**, the instantaneous tailpipe NO_x emissions, altitude, and speed profiles are also plotted. In addition, the NO_x threshold (h_{50}) is plotted as a horizontal-green-dashed line. For clarity, these figures show the measurements of only one test, because the other tests have similar patterns.

Figure 6.2 and **Figure 6.3** illustrate how generally high tailpipe NO_x emissions (peaks) are emitted during strong accelerations, which indicates high power demand. Logically, these accelerations are likely to be produced after every motoring, downhill, and stop (in urban) periods. Furthermore, a combination of uphill and acceleration lead to higher NO_x emissions, depending on SCR working conditions. On analysing the entire RDE test, the highest tailpipe NO_x emissions (peaks over NO_x threshold) occurred mainly in rural and motorway sections. For example, after the first urban part at ~900 s, where the SCR-inlet temperatures were low (around 200 °C) and SCR monolith is expected to be cold, the initial stage of the uphill led to the first subset of high peaks. These peaks matched the quick increase in SCR-inlet temperature. The second subset of high NO_x peaks (after ~1150 s), appeared during strong accelerations until the top height of the climbing stage at ~1400 s. Note that, after the first subset of NO_x peaks, the SCR-inlet temperature is at a much higher level (around 350 °C). Following this long climb, the long downhill stage cools down the SCR-inlet gas temperature to the lower levels. Meanwhile, the less grouped high peaks appeared during strong accelerations. Other subsets of high NO_x peaks occurred at ~2550 s with low SCR-inlet temperatures produced by a long downhill. Long motoring conditions are typical for the downhill. In these conditions, fuel-cut off and low power demand maximise the cool-down of the entire exhaust system because of the flow of the cold exhaust gas (Praveena and Martin, 2017).

The most significant subset of the tailpipe NO_x peaks were produced close to the lower altitude of the route (~ 3050 s) following a long downhill and because of the strong acceleration to reach motorway speed levels from a low speed of about 20 km h^{-1} . On the motorway, high deNO_x are expected; however, as shown in the figure, these peaks are produced under uphill and with the highest recorded SCR-inlet gas temperatures, that exceed 350°C . This corroborates that the highest NO_x peaks can occur outside the high-efficiency thermal window of the SCR device. From the air quality standpoint, these observations suggest that the population located at the base of the uphill or close to the high slope sections are more affected by vehicle's pollution; this was noted by (Triantafyllopoulos et al., 2019) for micro-environments such as highway entrance ramps and traffic lights.

Figure 6.2. Entire on-road test profiles of engine-out and SCR-inlet gas temperatures. The horizontal lines represent the low (200°C) and high (350°C) temperature references. Below: vehicle speed, altitude and tailpipe NO_x emissions. The NO_x thresholds (h_{50}) split 50 % of the cumulated emissions.

Figure 6.3 illustrates the h_{50} computed for the urban section. The figure shows that higher NO_x peaks are also present during strong acceleration and after motoring (deceleration or stop periods). Contrary to the rural and motorway sections, the SCR-inlet temperatures are generally low (near $\sim 200^\circ\text{C}$), which reflect different working temperature conditions for the SCR compared with the rest of the route. This suggests a separate analysis from other driving sections with a focus on the SCR operating temperatures.

Figure 6.3. Urban profiles for vehicle speed, altitude and tailpipe NO_x emissions. The NO_x thresholds split 50 % of the cumulated urban emissions. The urban part included the start ($t \leq 900$ s) and the end ($t \geq 4300$ s) of the RDE test.

6.4. NO_x emissions as a function of VSP

The VSP power usage and corresponding frequency during the RDE tests are summarised in **Table 6.1**; the computations of the VSP modes were stated in section 3.3.2.3. The vehicle was driven in a “normal power demand” ($\text{VSP} < 19 \text{ W kg}^{-1}$) most of the time, namely for 93 % of the RDE test and almost for the entirety of the urban section. Normal use-high power is low, with about 10 % and 2 % for the RDE and the urban part. However, high power usage ranges have a substantial effect on engine-out and tailpipe NO_x levels.

Table 6.1. Frequency and average deNO_x for VSP power usage level

Power usage	VSP range [W kg ⁻¹]	RDE		Urban	
		Frequency [%]	deNO_x [%]	Frequency [%]	deNO_x [%]
Deceleration	$\text{VSP} < 0$	24.7	84.5	26.5	85.9
Idle	$0 \leq \text{VSP} < 1$	22.5	89.9	41.7	89.4
Normal usage-low power	$1 \leq \text{VSP} < 10$	35.7	88.0	29.6	85.0
Normal usage-high power	$10 \leq \text{VSP} < 19$	10.2	87.0	2.0	84.1
Extra-high power	$\text{VSP} \geq 19$	6.9	83.5	0.1	74.8

Figure 6.4 shows the discretised values of engine-out and tailpipe NO_x emissions as a function of VSP, with their corresponding deNO_x percentage (with negative sign). The NO_x thresholds (h_{50}) for total and urban sections were also plotted as red-horizontal lines. The broad values of VSP were plotted in values of 2 W kg^{-1} to visualise the relationship between power and NO_x emissions. Note, that this figure does not represent the occurrence frequency, which is listed in **Table 6.1**.

The figure illustrates that engine-out NO_x emissions have a strong positive correlation with positive power ($\text{VSP} > 0$). However, the correlation between the increase in positive power and the deNO_x SCR performance is not clear. Positive VSP had an average deNO_x level of 87.0 % (s.d. 18.5 %) and 85.0 % (s.d. 16.8 %) for the RDE and urban sections, respectively. In general, **Table 6.1** summarises the urban deNO_x levels lower than the entire RDE levels, which can be attributed to lower working temperatures.

Low power under normal use has a greater average deNO_x than extra-high power and high power under normal use. Low power under normal use averaged deNO_x values of 88.0 % and 85.0 % for the RDE test and urban sections, respectively. A high power demand ($\text{VSP} \geq 10 \text{ W kg}^{-1}$) averaged deNO_x levels of 85.6 % and 83.6 % for the RDE and urban parts, respectively. This implies that higher tailpipe emissions for high power demand are caused by the positive correlation between VSP and engine-out emissions combined with the decrease in deNO_x levels.

The highest instantaneous tailpipe NO_x emissions, as represented by the observations above the NO_x threshold (h_{50}), are generated from the highest engine-out NO_x emissions and to a less extent from some outliers at lower VSP levels. For the entire RDE, the 67 % of observations above h_{50} are produced in the extra-high-power range ($\text{VSP} \geq 19$), and 92 % when the high power is included under normal use, i.e., $\text{VSP} \geq 10$. Both ranges correspond to 17 % of the driving time. In the urban section, 22 % of the observations above h_{50} were related to VSP values greater than high-power under normal use ($\text{VSP} \geq 10$) although it represents only 2 % of urban driving.

Figure 6.4. Boxplots of engine-out and tailpipe NO_x emissions with the corresponding deNO_x percentage as a function of VSP. NO_x thresholds split 50 % of cumulated emissions (a) entire RDE test (b) urban section; bins = 2 W kg^{-1} and the width does not represent the number of observations. Plots of NO_x emissions were trimmed at top to improve visualisation. Outliers of engine-out NO_x emissions were not plotted.

In **Figure 6.4a**, engine-out NO_x emissions show continuous growth, with a substantial increase under extra-high power ($\text{VSP} \geq 19$) usage. The tailpipe NO_x emissions are stabilised from $\text{VSP} > 28 \text{ W kg}^{-1}$. Further, it is reflected as an increase in the deNO_x performance that could be explained by an advantageous temperature operation, a steadier engine operation and a possible biased SCR control strategy; otherwise, higher tailpipe emissions can be released. These growing patterns between the tailpipe NO_x emissions and the VSP were reported previously (Varella et al., 2019). However, in their study, only three Euro 6c vehicles were tested, and they did not reflect a step-like profile

in tailpipe NO_x emissions as in this study, which shows a continuous increase in tailpipe NO_x emissions as a function of VSP.

The NO_x tailpipe outliers (green dots) represent an occasional deficit of NO_x conversion for each power bin. These outliers are also reflected as deNO_x outliers (grey dots) and are likely to appear at low power usage. These events are reflected as the typical peaks in urban and rural driving. **Figure 6.4a** and **Figure 6.4b** show that the amount of both types of outliers are diminished as VSP increases.

Although instantaneous NO_x emissions are lower in the urban section, distance-specific emission factors are dependent on speed, and therefore, the emission factors tend to increase in this section with the additional effect that vehicles move in a relatively enclosed area. This implies that, on average, more emissions per circulation area are emitted into the cities.

In summary, these results suggest that high tailpipe emissions are caused by engine-out NO_x emissions that depend on the power demand, with two cases: (a) the highest engine-out emissions with a high, but insufficient deNO_x level of the SCR system; and (b) not-so-high engine-out NO_x emissions with a particular or exceptional low deNO_x conditions of the SCR system.

6.5. SCR performance in real driving conditions

6.5.1. SCR-inlet gas temperature

Figure 6.2 illustrates clearly that the engine-out and SCR-inlet temperatures are not synchronised. The relationship between these exhaust gas temperatures is observed as a damped, delayed and time-dependent system caused by the transient heat transfer phenomena between the gas, exhaust system, and ambience, in addition to the strong influence of thermal inertia of the aftertreatment devices such as the turbocharger and DOC, among others. The figure, indicates that, first, a damped system owing to the reduction of extreme temperature values, particularly the highest temperatures. Further, low instantaneous exhaust gas temperatures peaks are smoothed. Second, it is a delayed system because instantaneous changes in the engine-out gas temperatures are not instantaneously followed downstream. As was noticed by Zhao et al., the transition between states of engine operating conditions takes less than 10 s, and the transition of the SCR system (temperature of the catalyst) is within minutes. This implies a temperature lag between the SCR's outlet temperature of 35 s, and 200 s to a change between the inlet temperature from 200 to 400 °C in the transient conditions tested in that study. Naturally, the distance between the engine and the SCR location impacts the effects here mentioned.

Figure 6.5 shows that the gas temperature entering the SCR system has a positive correlation with speed. In addition, urban driving is likely to produce SCR-inlet gas below 200 °C. The temperatures below 200 °C were 26 % and 40 % of the total and urban ($v < 50 \text{ km h}^{-1}$) driving time, respectively. The SCR-inlet temperatures above 350 °C are

produced at higher speeds than those in typical urban driving, and they represented the 10 % and 50 % of total and motorway ($v > 90 \text{ km h}^{-1}$) driving times, respectively.

Figure 6.5. Boxplot for exhaust gas temperature before the SCR system as a function of speed for the RDE tests

Along the exhaust system, the exhaust gas reduces its lowest and highest temperatures peaks, and it also reduces the average temperature value, particularly in the urban section. Thus, the 95th percentile for the engine-out temperatures was $523.3 \text{ }^{\circ}\text{C}$, while for the SCR-inlet gas temperatures it was $370.5 \text{ }^{\circ}\text{C}$. This fact can benefit the SCR system to avoid thermal sintering and thermal stress (Nova and Tronconi, 2014). Further, between the engine-out and SCR-inlet, the total average temperature was reduced from $297.0 \text{ }^{\circ}\text{C}$ to $245.8 \text{ }^{\circ}\text{C}$, and in the urban section, it was reduced from $240.3 \text{ }^{\circ}\text{C}$ to $206.5 \text{ }^{\circ}\text{C}$. This average value in the urban section is close to the minimum temperature that limits ammonia injection, which implies a potential cooling down of the SCR system with unfavourable conditions for the NO_x conversion.

6.5.2. Potential cooling down of SCR system in urban driving

The potential heat transfer from the SCR-inlet gas to the SCR system (W) using a reference level of $200 \text{ }^{\circ}\text{C}$, which means how much cooling power is in theory available to go below $200 \text{ }^{\circ}\text{C}$, was computed as

$$\dot{Q}_{200} = \dot{m}_{gas} \cdot C_{p_{gas}} \cdot (T_{SCR-inlet} - 200) \quad (6.1)$$

where, $\dot{m}_{gas}$ is the mass flow (kg s^{-1}), $C_{p_{gas}}$ is the heat capacity at a constant pressure of the exhaust gas, which is assumed to be equal to the $C_{p_{air@20^{\circ}\text{C}}} = 1054 \text{ J kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$, and $T_{SCR-inlet}$ is exhaust gas temperature before the SCR device. The heat not only takes as reference the minimum temperature that could lead to the inhibition of ammonia injection, but it is also a function of the mass flow entering the SCR system. From this equation, positive values represent the power that could potentially heat the SCR above $200 \text{ }^{\circ}\text{C}$. In contrast, negative values are the potential in the exhaust gas that could cool down the SCR system below this temperature level.

Figure 6.6 illustrates the engine-out and SCR-in gas temperature profiles of an urban interval; below, the potential cooldown of the SCR system, the tailpipe NO_x emissions and the deNO_x were plotted. The different driving modes—acceleration, cruise, deceleration, and idle—were included in the horizontal axis. The most remarkable result that emerges from these observations is that in urban areas, the flow of SCR-in gas with low temperatures frequently enters the SCR under acceleration when high engine-out NO_x emissions are generated. Note that while engine-out gas temperatures are considerably synchronised with the driving modes, the SCR-in gas temperatures are not. For instance, the periods between 5320–5340, 5640–5700, and 5870–5900 s present negative peaks for $\dot{Q}_{200}$, which implies a high potential heat transfer with temperatures below 200 °C and high mass flow, while acceleration occurs. Under these unfavourable conditions, NO_x emission peaks above the NO_x threshold emerged and the deNO_x values are also greatly diminished, thereby displaying low deNO_x peaks.

Figure 6.6. Comparison of engine-out and SCR-inlet exhaust gas temperatures, and heat power transfer of SCR-inlet temperatures, with 200 °C as a reference value.

The second-highest NO_x emission peak in the urban section appeared at ~ 5880 s. It occurred under the acceleration to reach 50 km h⁻¹, and after a prolonged period (~ 150 s) mostly in idle and with the SCR-inlet temperatures below 200 °C. In fact, the period with temperatures below 200 °C started at about 250 s before 5620 s. This example, similar to the peak at 5330 s, reflects the working conditions with congestion or long retentions that are common to urban driving, and it strongly affects the SCR performance. The next peaks, between 5930–5980 s can appear because of the low temperature of the SCR monolith after the long cooling down periods, and without sufficient heat transferred from the exhaust gas to reach the thermal window. Note the deNO_x peaks (grey) present between 5650–5750 s for the low entering temperatures.

The time and energy of the potential cooling down ($-\dot{Q}_{200}$) is listed in **Table 6.2**. In general, energy is the integral of power, computed as: $Q_{200} = \sum \dot{Q}_{200} \cdot \Delta t$, where Δt is

the sampling time equal to 1 s. The table shows that in the urban section about 40 % of the time, the SCR-inlet temperature was below 200 °C with a notable change in the occurrence frequency for an acceleration mode from 1.6 % for the engine-out to 9.2 % for the SCR-inlet. The ratio between these percentages (5.8:1) is higher than other driving modes, and it supports the observations in **Figure 6.6**.

Table 6.2. Percentages of urban temperatures below 200 °C and potential energy for cool down energy

Driving mode	Engine-out temperature (time) [%]	SCR-inlet temperature (time) [%]	–Q200 (energy) [%]
Acceleration	1.6	9.2	34.0
Cruise	1.6	4.0	9.5
Deceleration	4.6	7.1	13.3
Idling	22.9	19.2	43.2
Total urban	30.7	39.5	100.0

Regarding energy, the acceleration mode comprised 34 % of the energy because of the increase in the mass gas; however, idling still shows a higher potential for cooling down with 43.2 % of that energy. The other modes—cruise and deceleration—have a lower potential of about 23 % of the energy. (Gao et al., 2019a) proposed an approach to heat the DOC inlet gas only during low levels and in cut-off conditions; however, it was not successful to improve the deNO_x of the SCR system located downstream. It occurs due to the cooling of the SCR system in motoring, with the high probability of acceleration after those events. It suggests that careful thermal management and possible independent heating should be implemented for the SCR system. Both elements must consider the working conditions under acceleration. The theoretical heating of the exhaust gas to maintain a minimum temperature level is discussed in section 3.6.

6.5.3. SCR efficiency as a function of SCR-inlet gas temperature and mass flow

Figure 6.7 exhibits the discretised values of engine-out and tailpipe NO_x emissions as a function of the SCR-inlet gas temperature, with their corresponding deNO_x percentages (with negative sign). The NO_x thresholds for HES-50 were also plotted to identify the highest NO_x peaks. **Figure 6.7a** shows two remarkable results related to the SCR performance under the real-driving test. First, the deNO_x performance is reduced outside of SCR's thermal window, at the lowest and highest SCR-inlet gas temperatures. Second, the higher tailpipe NO_x peaks emissions are correlated with higher SCR-inlet temperatures (over 370 °C), which is caused by the high engine power release and high engine-out gas temperatures. These results are consistent with the results of the Section 5, where NO_x emissions peaks for 50 % of total emissions were analysed as a function of tailpipe exhaust gas temperature. About 40 % of the observations were under urban temperatures, and ~35 % occurred in the narrow highest temperatures range of the motorway section.

Figure 6.7. Boxplots of engine-out and tailpipe NO_x emissions with the corresponding deNO_x percentage as a function of SCR-inlet gas temperatures. NO_x thresholds split the 50 % of cumulated emissions (a) entire RDE test (b) urban section; bins = 5 °C. Outliers of engine-out NO_x emissions were not plotted.

In the case of the entire RDE tests, observations above NO_x threshold correspond to these highest emission peaks that could not be entirely reduced by a moderate deNO_x reduction at high SCR-inlet temperatures. Further, several outliers cross the NO_x threshold in the entire range of measured temperatures. The urban section corresponds with lower temperature bins (< 290 °C), and the emission peaks match outliers in the urban temperatures below 260 °C. Similar to the analysis of VSP, the outliers of deNO_x (grey dots) are diminished as the temperature increases; this implies that low SCR operating temperatures are the cause of emission peaks at low power demands.

Figure 6.8 shows the deNO_x percentage for different ranges of SCR-inlet gas temperature. The bins represent the gas mass flow in values of 5 g s⁻¹. The deNO_x is favoured in the temperature window between 220–340 °C. The average RDE deNO_x levels were 82.8 %, 91.7 % and 85.5 % for SCR-inlet gas temperatures below 220 °C, within 220–340 °C, and above 340 °C, respectively. For the urban section, the average deNO_x levels of 81.8 % and 90.4 % resulted for temperatures below and above 200 °C, respectively.

Figure 6.8a shows a new important result: deNO_x reduction is more dependent on mass flow when the gas temperature is outside of the temperature window (200–350 °C). In the case of the urban section, which is characterised by low operating temperatures, **Figure 6.8b** shows this behaviour only on the bottom side of the temperature window (<200 °C). These results confirm previous findings of (Zhao et al., 2011), wherein the amount of ammonia storage was found to be a key parameter for correct ammonia injection, which is essential to the trade-off between maximum efficiency and minimum ammonia slip.

a)

Figure 6.8. deNO_x performance as a function of the exhaust gas mass and temperature entering the SCR.
Bins = 5 g s⁻¹; red dots = bin mean

In transient processes, the higher effect of temperature rather than flow rate on ammonia storage explains the SCR behaviour depicted in **Figure 6.8** (Praveena and Martin, 2017; Zhao et al., 2011). This means that high deNO_x rates at favourable temperatures are independent of gas flow. On the one hand, the amount of ammonia storage on the surface of the catalyst has more influence on deNO_x performance as the temperature decreases, and in particular, for low exhaust temperatures below 280 °C (Zhao et al., 2011). Therefore, in this case, high flow gas decreases the NO_x conversion. This implies that under urban driving, the patterns shown in **Figure 6.8** with low SCR-inlet temperatures combined with high mass flow under accelerations (where high engine-out emissions are expected) produce the best scenario for the production of high NO_x emissions or emission peaks.

On the other hand, above 320 °C, the early arrival of ammonia slip increases by the influence of flow rate and improper control of ammonia storage (Zhao et al., 2011). This

is showed for the RDE section in **Figure 6.8a** for temperatures above 360 °C, with the consequent reduction of deNO_x and the negative influence of gas flow in the deNO_x level. Finally, outside the thermal window, the emission of NO₂ is promoted, and its formation occurs at low (<200 °C) and high (>450 °C) temperatures via the formation of surface species such as NH₄NO₃ and NH₃, respectively (Guan et al., 2014).

These findings justify the necessity for heating the SCR, at least to solve deNO_x reduction by low operating temperatures. A simple choice to reduce the SCR light-off time, and therefore the low temperatures, is to decrease the thermal inertia of the catalyst and move the SCR upstream closer to the engine (Miao et al., 2009). This has been implemented in new diesel cars. However, excessive temperatures must be avoided to maintain the catalyst lifetime and efficiency, as shown in the results of this study.

6.6. Chapter conclusions

The main findings of this chapter lead to the following conclusions:

The highest tailpipe NO_x emissions, represented as NO_x peaks, are a significant part of the total NO_x emission. However, because of its low occurrence, their prediction and characterization become difficult. For instance, 50 % of cumulated emissions occurred in only 2.6 % and 4.7 % of the total and urban driving time, respectively. According to the results, the VSP is positively correlated with the engine-out NO_x emissions, which then cross the SCR system. Thus, the high tailpipe emissions are caused by two possible situations: (a) the highest engine-out emissions with a high, but not optimal deNO_x level of the SCR system, and (b) not-so-high engine-out NO_x emissions with a particular or exceptional low deNO_x conditions of the SCR system. The reasons for the deNO_x decrease are supported in the following conclusions.

There is a temperature window for the SCR-inlet gas temperature between 220–340 °C, where deNO_x is favoured. The average RDE deNO_x levels were 82.8 %, 91.7 % and 85.5 % for SCR-inlet gas temperatures below 220 °C, within 220–340 °C, and above 340 °C, respectively. For the urban section, the average deNO_x levels of 81.8 % and 90.4 % were obtained for temperatures below and between 200–290 °C, respectively. In addition, outside that temperature window, the deNO_x becomes more dependent on the mass flow, with a lower conversion for higher mass flow. Low temperatures are typical of urban driving, given that for 40 % of the time, it was under 200 °C. In the rural and motorway sections, the lowest temperatures were measured after long motoring (downhill). Higher temperatures are typical of motorway driving, with 50 % of the time over 350 °C. Therefore, under these high-temperature conditions, a possible cooling down of the SCR system can be advantageous for rural and motorway driving. However, this option has not been yet analysed in the literature.

For low SCR-inlet temperatures, they not only reduce the SCR performance but can lead to inhibition of ammonia injection for SCR-inlet < 180 °C. Therefore, a minimum level of 200 °C was selected as the reference level in this study. The theoretical amount of heat below 200 °C that can be transferred from the SCR monolith to the SCR-inlet gas results

in 43 % of energy during idling; against intuition, 34 % of the energy during acceleration; and the remaining 33 % of energy during deceleration and cruise modes. These results are explained by the unsynchronised change in the temperature between the engine-out level and SCR-inlet level. The SCR-inlet temperature obeys the transient heat transfer and the thermal inertia of the exhaust elements. For the tested vehicle, the SCR was located close to the DOC, which reduces the phenomena described here. This phenomenon was useful to explain the highest tailpipe NO_x peaks in the urban section. These peaks occurred during acceleration (high power demand), and were often lower than the SCR-inlet gas temperatures with the high mass flow that cooled down the SCR, with the additional deNO_x drop. Furthermore, the acceleration follows the cooling-down conditions of the cruise-deceleration-stop driving sequence.

Owing to the complexity of the new aftertreatments and powertrains, this study shows the importance to model and analyse the NO_x emissions of modern vehicles as two blocks: one for the engine-out emissions (NO_x emitter) —mainly dependent of power demand— and another block, for the SCR system (deNO_x device), for which its performance is related to the exhaust gas flow and temperature. Thus, the NO_x emission peaks could be predicted more accurately.

CHAPTER 7

Influence of high NO_x emissions on microscopic models: Case of a SCR diesel vehicle

Deterministic models are of the ‘causal’ type, and their prediction depends on the conditions to accomplish usually simplified assumptions used in the model formulation. Although they have a substantial degree of explanatory power, instantaneous NO_x emission requires the modelling of engine-out values, and the additional modelling of the aftertreatment when this system changes the performance according to complex operating conditions, e.g. in SCR-equipped vehicles. The NO_x emission peaks emerge as a high nonlinear function of time or other parameters. On the other hand, statistical models are of the ‘non-causal’ type, establishing semi-empirical relationships between the data and outputs. In this field, machine learning algorithms have shown high potential to solve nonlinear problems. Therefore, they are proposed as an alternative tool to improve prediction accuracy. This chapter compares three approaches: PHEM (physics-based), EOVM-ML (random forest), Hybrid (PHEM + random forest). In the case of a hybrid approach, it combines a physics-based model such as PHEM, with a machine learning algorithm. The results obtained using PHEM are used as input for the training of the RF algorithm. It is intended to combine the best attributes of the deterministic and the data-driven based models.

7.1. Machine learning modelling

7.1.1. Selection of input variables

In general, for the prediction of emissions, powertrain variables such as engine speed, manifold absolute pressure, and engine power show a higher explanatory capabilities than driving variables such as vehicle speed, acceleration and road grade. However, powertrain variables—also named IOVs—are usually more difficult to obtain or model (Frey et al., 2010). Therefore, the driving variables, also called EOVs can be obtained or modelled from traffic and topographical profiles, and it becomes useful for emission estimation as input for microscopic emission models such as PHEM, CMEM, MOVES, and AVL Cruise. However, the action of aftertreatments has diffculted the prediction of NO_x emissions. In the case of SCR, the deNO_x performance of the SCR is strongly dependent on the temperature and mass flow of exhaust gases. Therefore, to improve modelling of NO_x, not only IOVs or EOVs, but also other parameters related to the thermal management of the after treatment system must be included in NO_x prediction (Fernandes et al., 2019). PHEM uses exhaust gas temperatures and space velocity to create the SCR conversion maps; however, the estimation of this variables requires the thermal modelling of the aftertreatment (a 0-d thermal model in PHEM), which involves measurements and characterisation of the layout of the aftertreatment elements. To

avoid this extensive work and achieve simplification and generalisation of the models, the thermal model is replaced by a machine learning algorithm in the case of the Hybrid model. The other modelling approach for this chapter is a pure machine learning model that uses EOVs as inputs to predict tailpipe NO_x emissions; this model is called from now EOV-ML model.

The driving cycle is the source of EOVs as predictors for emission models. To develop the model using machine learning algorithms, a set of input variables was selected and created. Instantaneous emissions can be affected by past events (Qi et al., 2004). For example, (Pan et al., 2019) used Boosted regression trees and (C. Wang et al., 2018) used neural networks, that are models that use the past states of EOVs as VSP, speed and acceleration. Although temperature and mass flow of exhaust gases are key elements for SCR efficiency, these variables were correlated with average speed and VSP, respectively (Chapter 6). Further, the exhaust gas temperature at SCR-inlet corresponds to a dynamic system delayed with respect to the engine-out exhaust gas temperature; see Chapter 5. Therefore, this study uses the past values of the EOVs to learn the patterns of the aftertreatment behaviour in a non-parametric machine learning algorithm. The estimation model for the EOV-ML model takes the form

$$\text{NOx}_t^{tp} = f(\text{VSP}_\tau, v_\tau, a_\tau, \alpha_\tau) \quad (7.1)$$

where t denotes time, NOx_t^{tp} is the tailpipe NO_x emission at the current time t , v is the speed, a is the acceleration, and α is the road grade. For all predictors, the sub-index τ , denotes the set of observations for the current and past times (s), and therefore, $\tau = \{t, t-1, t-2, t-5, t-10, t-30\}$.

In the case of the hybrid model, the same variables and the engine-out NO_x emissions come from the PHEM simulation. The machine learning part for the hybrid model takes the form:

$$\text{NOx}_t^{tp} = f(\text{NOx}_\tau^{eo}, \text{VSP}_\tau, v_\tau, a_\tau, \alpha_\tau) \quad (7.2)$$

where t denotes time, NOx_t^{tp} is the tailpipe NO_x emission at the current time t , NOx_τ^{eo} is the engine-out NO_x emission for τ times. Thus, the total number of predictors were 24 and 30 for the EOV-ML and hybrid models, respectively.

7.1.2. Selection of the prediction algorithm

Every learning algorithm adjusts the optimal internal parameter to match the training data to the outputs through the prediction algorithm. However, some characteristics were considered to select the candidate algorithm for this investigation:

- The number of hyperparameters, which simplifies the tuning of the model. It influences the number of repetitions to obtain the best hyperparameters, thereby reducing the computational power needed to train the model. The data had 24–30 predictors and approximately 12000–13000 observations.

- To avoid overfitting, it is important to generalise the model. Although RDE tests had comparable driving dynamics, real-world conditions change instantaneous operating conditions and influence on the variability of tailpipe NO_x emissions.
- The performance, as the capacity of the model to solve difficult and nonlinear problems is required to predict NO_x emission peaks.

From the comprehensive source of state-of-the-art machine learning algorithms, **Table 7.1.** lists the possible algorithms for building the emission models. Since the objective is to evaluate the accuracy of the tailpipe NO_x predictions, without explaining the relationship with the predictors, the algorithms with high prediction accuracy but low interpretability were selected as candidates. All models from the table are black-box type with low or no interpretability.

Table 7.1. Comparison of predictive modelling algorithms

Prediction method		Tune parameters*	Advantages	Disadvantages
Random forests (RF)	1	method = 'rf'	<ul style="list-style-type: none"> · Robust to overfitting · Great at learning complex, highly non-linear relationships · Provide a reliable feature importance estimate 	<ul style="list-style-type: none"> · An ensemble model is less interpretable than an individual decision tree · Training a large number of deep trees requires high computational costs · A large number of trees may make the algorithm slow for real-time prediction
eXtreme gradient boosting (XGBoosting)	4	method = 'xgbLinear'	<ul style="list-style-type: none"> · Faster than other implementations of gradient boosting · High-performance algorithm 	<ul style="list-style-type: none"> · Training takes longer because trees are built sequentially
	7	method = 'xgbTree'	<ul style="list-style-type: none"> · efficient use of hardware resources · Best-in-class for small and medium structured/tabular data 	<ul style="list-style-type: none"> · More sensitive to overfitting if the data is noisy
Support vector machines (SVM)	1	method = 'svmLinear'	<ul style="list-style-type: none"> · Less overfitting and robust to noise · No local minimal 	<ul style="list-style-type: none"> · Computationally expensive · Lack of transparency of results
	3	method = 'svmPoly'	<ul style="list-style-type: none"> · Good for generalisation 	<ul style="list-style-type: none"> · Selection of kernel function
Neural networks (NN)	3	method = 'neuralnet'	<ul style="list-style-type: none"> · Strong in generalisation ability · Flexible in learning almost any kind of feature variable relationships · Efficient for online learning 	<ul style="list-style-type: none"> · Limited ability to explicitly identify possible causal relationships · Prone to overfitting · Needs many samples to deliver high accuracy

Adapted from (Li et al., 2017) and other sources. *The tune hyperparameters corresponds to available parameters in caret package for R (Kuhn, 2008).

Random forest (RF) (Breiman, 2001) was used for this study because it requires fewer tuning parameters and is a powerful ensemble model for non-linear problems. (Breiman, 2001) proved that RF are protected from overfitting; therefore, the model will not be adversely affected if a large number of trees are built for the forest. In addition, several variables are inputted in the model and RFs provide a reliable feature importance estimate. The RF is user-friendly, as there is no need to define complex relationships between predictors. In the caret package, RF has only one tuning parameter: the number of predictors randomly sampled as candidates at each split (*mtry*). Breiman (2001) recommends setting *mtry* to one-third the number of predictors for regression tasks. Other important hyperparameter is the number of trees to grow in

the forest (*ntree*) that affects the accuracy of the model and becomes stable after a certain value. The caret package only focuses on hyperparameters with a major influence on algorithms performance (Kuhn, 2008); therefore, it only tunes *mtry* and uses *ntree* = 500 as default. For this study, *ntree* = 1000 was used to improve accuracy; however, a high computational effort was required for training the models.

7.1.3. Model train and tune

Three RDE trips were measured; therefore, two tests were used for training and tuning the machine learning algorithms and to create maps in PHEM. Then, the final tuned models or the PHEM resultant models were tested in the remaining RDE test. It warrants that the training or map creation is conducted over 65–68 % of the total data from the measurement campaign.

Figure 7.1. Example of tuning the *mtry* hyperparameter using 3-repetition 5-fold cross validation for random forest models (a) EOVM-ML model and (b) hybrid model

To tune the machine learning models, 5-fold cross validation was used and repeated three times. The choice of *k* for *k*-fold cross validation is usually 5 or 10; however, there is no formal rule (Kuhn and Johnson, 2013). The 5-fold validation was selected to increase the probability to catch the NO_x emission peaks into the training sets because observations containing NO_x peaks are infrequent. The repetition of the validation process is used to reduce the probability of overfitting, although it requires more computational power (Raschka, 2018). For tuning the RF models, the grid-search method was selected to search the best hyperparameters for the *mtry* variable. The grid-search method demands highly computational power but can provide a good image when the number of hyperparameters and the number of predictors are not very high (Kuhn and Johnson, 2013)

Figure 7.1 shows an example of the accuracy for a sequence of *mtry* values for the training of the RF algorithms. The best *mtry* values for all models were between 3–5 and 5–12 for EOVM-ML and hybrid models, respectively. The training, validation, and tuning computation times were between 20–80 min, depending on the size of the grid search and the *mtry* level. The computation was performed in the Amazon elastic compute cloud

on an instance with 36 CPUs and 72 GB of RAM. This demonstrates the high computational cost for the training of RDE tests for RF with the selected predictors and the validation process. However, once the model is built, the execution of the models was less than 1 min in a personal computer. The execution of a model in PHEM takes about 10 s. The best tuning parameters were automatically used to create the final model using all training data (two RDE trips). It is important to note that every model corresponds to a unique specific combination of predictors and observations, and which patterns were learned into the trees. The cross validation and repetition give the opportunity to generalise the model. Therefore, the accuracy decreases for higher *mtry* than the best-case, which is likely due to over-fitting.

7.2. Model comparison and NO_x high emission sets

After the training (machine learning) or the emissions and SCR conversion maps creation (PHEM), each model was tested in the no-train RDE trip, using the absolute EFE, RMSE and R² as metrics for the tailpipe NO_x predictions; Section 3.3.4. **Figure 7.2** presents the comparison between model approaches investigated in this chapter. Bars show average metrics for tailpipe NO_x prediction, light-blue dots are RMSE for the engine-out NO_x results from PHEM, and the black dots represent the relative frequency of each HES observations.

Figure 7.2. Comparison of NO_x predictions. For the different HESs, bars represent the average metrics for the predictions. |EFE| is the absolute emission factor error (%), R² (%), and RMSE (mg s⁻¹). Error bars = +1 standard deviation. HES = 100 represent the entire RDE trips. Time in PHEM plot represents the relative frequency of every HES set.

It is important to note that HES-100 had an NO_x threshold of 0 mg s⁻¹, which means that all predictions of the entire RDE trip are evaluated. Therefore, the total RDE trips predictions show that the hybrid approach slightly outperformed the EO-V-ML model. Further, the results of this last approach showed better results than the PHEM simulations. The prediction error of the total emission factors averaged 48.0 % (s.d. 30.3) for PHEM, 34.0 % (s.d. 31.0) for EO-V-ML, and 30.5 % (s.d. 27.4) for the hybrid models. For the instantaneous error predictions, RMSE (in mg s⁻¹) averaged 8.14 (s.d. 2.33), 3.96 (s.d. 0.42), and 3.85 (s.d. 0.41) for PHEM, EO-V-ML, and hybrid models, respectively. The highest coefficient of determination (R²) of 0.51 was for the hybrid model, followed by values of 0.49 and 0.18 for the EO-V-ML and PHEM models. The prediction errors found

in this study are in the same range of those in the literature; however, NO_x predictions of all studies present high variability and detailed information of Euro 6b SCR-diesel passenger cars modelling is not available. In the comparison of the micro-scale modelling of Euro V bus and coaches in Hong Kong (Wong et al., 2019), the NO_x predictions resulted in an R^2 for PHEM and PDP to be respectively equal to 0.18–0.36 and 0.24–0.52 for the bus, and 0.38–0.52 and 0.49–0.58 for the coaches. In that study, PHEM was not used with the aftertreatment simulation, and R^2 was recalculated as the square of Pearson correlation coefficient (r). In (Pan et al., 2019), the GBRT algorithm was compared with VT-micro model for Euro III, IV diesel vehicles, liquefied natural gas (LNG), and hybrid vehicles. The average results for NO_x predictions showed an RMSE of 87 and 73 mg s^{-1} for VT-Micro and the developed model, respectively. In (C. Wang et al., 2018), the NN used for the prediction of buses with different powertrain technologies showed average RMSE of 92 and 167 mg s^{-1} and R^2 of 0.78 and 0.66 for the NN and polynomial regression methods, respectively.

Regarding the NO_x emission peaks, those peaks are represented and clustered into the HES-L data sets. The NO_x thresholds (h_L) and the percentage of time of every HES are tabulated in Annex B. **Figure 7.2** (in PHEM model plot) shows the low occurrence of this highest NO_x emission events measured in tests. For the tested vehicle, in real-world conditions, there is a nonlinear relationship between the percentage of time for each HES and the HES number (L), which represents the percentage of total emissions. Considering the biggest change in the occurrence of the HESs, the HES-90 set would characterise the tested vehicle with a NO_x threshold, $h_{90} = 1.1 \text{ mg s}^{-1}$. The HES-90 set represented in average the 16.4 % of the total driving time, accounting for 90 % of the NO_x emissions. The low occurrence of NO_x peaks makes instantaneous NO_x emission prediction difficult because most data have lower emission levels. If the model uses emission maps or uses a simple parametric statistical model, the “average” NO_x value will be increased by the NO_x peaks (outlier). In this case, the generalisation accuracy of the model should be based on the correct representativity of the characteristic real-world driving conditions by the training data.

Figure 7.3 shows the instantaneous tailpipe predictions for the models at different time-lapses; as a reference, the previous analysis with the same data was done in section 6.3 for the tailpipe NO_x emissions, speed, and road grade. The figure shows that NO_x peaks are predicted at the correct occurrence point; however, the magnitude had an imprecise prediction. PHEM tends to produce higher peak levels than the other models (for this testing route). This aspect can explain why PHEM has better emission factors for the HESs with high NO_x levels rather than lower levels. Because the instantaneous NO_x emission values depend on NO_x concentration and mass gas, both terms can be investigated in PHEM and most experienced users can improve the creation of SCR conversion maps. The EOVM-ML and Hybrid models have similar prediction patterns, which are slightly improved by the hybrid model as shown by the results in **Figure 7.2**.

Figure 7.3. NO_x predictions (a) change from urban to rural driving, (b) observations with the highest NO_x emissions of the trip (c) urban part at the end of the test. Please see Section 6.3 for a detailed description.

Figure 7.3a illustrates the long time-lapse of high emission peaks produced during the change from the urban section to a rural section and the start with a strong uphill at 900 s and with the downhill at 1400 s. The first highest NO_x peaks (from 950–1030 s) are not followed by any of the models because of a low SCR-inlet temperature, which produces atypical observations, with patterns that cannot be learned by the models and would not be characterised in the emission maps of PHEM. The following events with high NO_x peaks (1170–1350) also had incorrect levels; however, for these events, the SCR-inlet temperature was high. The main reason for the inaccurate prediction of NO_x peaks is their low occurrence and the low probability to be represented into the model.

Figure 7.3b shows the section with a sequence of the highest NO_x peaks of the entire trip, which occurred between 3080–3650 s during motorway driving. PHEM demonstrates a more changing behaviour, and therefore, the highest emission peak (3080 s) is overestimated by 3.3 times using PHEM. This behaviour provides a better estimation of the peaks at 3600–3650 s; however, with overestimation of some previous observations starting at 3300 s. Lower emission levels are illustrated in **Figure 7.3c**. It corresponded to an urban section, where SCR-inlet temperatures were close to 200 °C. All models show a better prediction than other sections, with a little tendency to overestimate the magnitude of the peaks. Since urban sections represent about one-third of distance but about one-half of driving time, the data has more probability of being learned in the models. In the case of PHEM, NO_x peaks (outliers) can increase the “averaged” value for the bins of the emission and conversion maps. These results support the possible advantage of separating the prediction of high emission peaks from the rest of the observations.

Owing to the low frequency of the highest NO_x emissions, the creation of the modelling approaches of this study tends to predict better low NO_x emissions. EFE and RMSE decrease as R² increases when the HES-L sets ranges from L = 10 to L = 100. Therefore, HESs with high NO_x thresholds are worse predicted, except for PHEM. In general, improving the instantaneous prediction of NO_x peaks reduces the total error. Thus, the prediction of “low” emission levels is reflected in the instantaneous error metrics as RMSE, while the prediction of the high peaks affects the EF error.

From the results emerge the possibility that the prediction of NO_x emissions can be performed with two main data sets, one for the HES observations and one for the remaining “low” NO_x emissions. The first step must be providing a strong definition of HES. Then, a classification model would predict the occurrence of ‘high’ emissions. Thus, the HESs, and the complementary low emission set (LES) would be predicted in separate regression models to be later merged in a final prediction result. To provide a criterion to separate HES and LES, the change in the percentage of time for each HES was established in a previous paragraph. However, a criterion based on the change in the prediction accuracy as the HES percentage increases is more appropriate. **Figure 7.4** shows the difference in the error metrics for each increment of HES from 10 % to 100 % of total emissions. The higher differences (changes in error metrics) are possible cut

points to separate HESs and LES sets for the posterior using in the classification task (**Figure 7.4**).

For PHEM, the biggest change in R², EFE and RMSE errors is for the change at HES-100, which means that HES-90 and the complementary dataset, LES-10 (the 10 % of emissions with the lowest instantaneous NO_x emissions) are appropriate to build separated models. This indicates on average, a split of 16 % and 84 % of data for HES-90 and LES-10, respectively. For the EOVM-ML model, the biggest differences are at HES-80, HES-100, and HES-20 for EFE, R², and RMSE, respectively. However, a “good averaged” difference can be selected considering the instantaneous error metrics at HES-20 or a more representative dataset for the high NO_x emissions at HES-100. In general, HESs represent low occurrence; therefore, bigger HES sets are preferred to have more information for the training tasks. Therefore, the selected cut-point for the separated models is HES-90. In the case of the hybrid model, the differences are slightly lower than EOVM-ML modelling because in general terms the hybrid model has better performance, and similarly, a possible cut point can be selected for HES-90. The improvement in the model accuracy by separating HES and LES datasets needs further investigations considering the feature selection and algorithm comparison in the case of machine learning approaches.

Figure 7.4. Difference of a prediction metrics values compared to the next higher HES bin. HES = 100 represent the entire RDE trips. EFE error (in %), R² (in %), and RMSE (in mg s⁻¹)

In PHEM, the engine-out NO_x emissions are relatively more accurate than tailpipe emissions. First, the RMSE error of engine-out NO_x predictions appear to be similar (in the same order of magnitude) to the tailpipe predictions. For HES-100, the RMSE errors were 12.36 mg s⁻¹ (s.d. 2.08) and 8.14 mg s⁻¹ (s.d. 2.33) for engine-out and tailpipe emissions, respectively. However, engine-out NO_x emissions have higher variability than the tailpipe ones; therefore, a bigger RMSE would be expected. For engine-out and tailpipe NO_x emissions, the measured 5–95th percentiles were 0.01–6.90 mg s⁻¹ and 0.31–43.76 mg s⁻¹, respectively. Second, the hybrid model showed more accurate results because it uses the NO_x engine-out predictions from PHEM. Since PHEM and hybrid models use engine-out NO_x predictions in a second step to predict tailpipe emissions, these results lead to the conclusion that the PHEM’s exhaust simulation exhibited an inferior performance than that of the random forest for the same purpose. The machine-

learning algorithm could represent the non-linear relationships between inputs and the output (tailpipe NO_x emissions) of the SCR model more accurately.

7.2.1. Variable importance

Figure 7.5. shows the variable importance for the machine learning models as computed by the caret package during the training and tuning processes. For the final EOVM-ML models, the most important variables were in the following order: $VSP_t > VSP_{t-1} > VSP_{t-2}$. Their importance levels were 100, 40–58, and 34–38, respectively. Below these predictors, α_t, a_t, VSP_{t-5} alternated in the 4–6th place. The other predictors for the acceleration in past events were at the bottom of the importance evaluation; this could be explained by their correlation with VSP. There was no clear difference between the variable importance of the remaining predictors. This implies that all predictors could be useful for the accuracy of EOVM-ML models. These results denote the well-known relationship between power and pollutant release. For the RF models, the power and previous events are powerful explanatory variables for NO_x emission modelling as noted in earlier the works (Pan et al., 2019; C. Wang et al., 2018) A feature selection procedure could be further investigated. From the present investigations, a simpler model can be built by removing past events of acceleration.

Figure 7.5. Example of variable importance results for random forest models (a) EOVM-ML model (b) hybrid model. The variable importance is scaled to 100.

For the final hybrid models, the most important variables were in the following order: $NOx_t^{eo} > VSP_t > NOx_{t-1}^{eo} > VSP_{t-1}$. The importance was between 100, 70–82, 30–57, and 18–40, respectively. As the case of EOVM model, there was not a clear difference between the variable importance of the remaining predictors. VSP and engine-out NO_x show a sufficient explanatory power to link engine-out with tailpipe NO_x emissions and to “replace” a thermal and conversion model of the aftertreatment layout with SCR. Because the differences between the EOVM and hybrid models is not large, the accuracy of tailpipe emissions does not depend on a great extent on the accuracy of PHEM engine-out maps.

7.3. Chapter conclusions

The main findings of this chapter lead to the following conclusions:

A comparison between different model approaches (a) based on the driving dynamics and vehicle modelling (PHEM), (b) based on external operating variables (EOVs) and random forest (EOVM), and (c) based on PHEM for the prediction of engine-out NO_x emissions and a posterior use of RF to predict tailpipe emission (Hybrid) led to the conclusions that Hybrid models were better than EOVM, and these last models outperformed PHEM. However, the selection of an applicable model for a determined objective in the environmental research and policy decision requires considering other aspects such as interpretability, capability to link to meso and macro models, ability to represent a fleet of vehicles, simplicity, computational effort, ability of an offline training, size of the model, amount and availability of the input data, among others.

The high NO_x emissions—displayed as emission peaks in instantaneous emission plots—represent a large amount of total emission within a small percentage of observations. These characteristics are reflected as high non-linear behaviour and hard predictability for micro-emission models. The results show that the prediction of NO_x emission peaks is key to improve the accuracy of every model, and a separate analysis from the remaining “low” NO_x emissions could improve the total prediction power of models. Owing to the high occurrence, the accuracy in the prediction of “low” emission levels produces good instantaneous error metrics as RMSE, while the correct prediction of the high peaks provides less error in EF values by the low occurrence and the high impact in the total emissions.

Since the hybrid model uses PHEM as a basis for the tailpipe predictions, the arduous work of aftertreatment dimensioning, characterisation and simulation for an SCR-equipped vehicle is replaced by a machine learning algorithm. However, although the hybrid approach shows better accuracy than PHEM, the black-box model used to estimate tailpipe NO_x has limited interpretations; therefore, outside the boundaries of the used predictors, the predictions are not guaranteed. In addition, the building of an “average” vehicle of the fleet is not plausible. This strategy is used by HBEFA to obtain emission inventories based in PHEM as micro emission and traffic situations to represent driving patterns.

The analysis of the variable importance shows that the addition of engine-out NO_x emissions improved model accuracy. However, EOVM-ML models show that EOVMs as predictors lead to accurate prediction of tailpipe NO_x emissions. A deeper predictor selection analysis may be useful for machine learning models.

8. Conclusions and future works

8.1. General conclusions

The general conclusions are linked to the research questions and hypothesis of this thesis and are described below.

Research question 1

What are the real-world NO_x emission levels for the different Euro-6b vehicle technologies?

This study demonstrates that the real-world NO_x emission levels can be below or above Euro 6 limits according to the combination of powertrain, fuel injection approach and aftertreatment used; further, the control of every system and thermal management of aftertreatments impact tailpipe NO_x emissions. These aspects are explained in depth by the following hypothesis.

Conventional diesel vehicles require SCR systems to satisfy real-world Euro 6 emission limits. Gasoline direct injection vehicles require (a) diesel-like aftertreatment systems, or (b) to meet stoichiometric combustion in all driving conditions. The SCR-diesel and HEV vehicles can improve the aftertreatment thermal management to further exploit their potential for pollution reduction, particularly in urban areas. Therefore, to comply with post-Euro-6 regulations, these vehicles should be equipped with heating or indirect thermal management with an optimal trade-off between pollution reduction and fuel-economy penalty.

Hypothesis 1.1

Hot-start NO_x emission levels in RDE tests from Euro-6b vehicle technologies depend on the fuel and aftertreatment technologies.

Yes, more precisely, hot-start NO_x emission levels depend on the combination of powertrain, fuel injection, and aftertreatment type; see Sections 4.4 and 6.1. The diesel vehicles equipped with one SCR (tested in Madrid and Graz) showed reduced emission levels compared with the other diesel vehicles with LNT and only-EGR NO_x control systems. On average, the raw distance-specific emission factors for on-road tests were 1.3 (s.d. 0.32), 1.0 (s.d. 0.50), 7.4 (s.d. 0.69), and 9.0 (s.d. 0.26) times the Euro 6 limit for the SCR (Graz), SCR (Madrid), LNT, and only-EGR diesel vehicles, respectively. In urban driving, for the same vehicles, the emission factors averaged 1.4 (s.d. 0.37), 1.6 (s.d. 0.13), 6.3 (s.d. 0.67), and 4.8 (s.d. 0.36) times Euro 6 limit, respectively. Urban emissions of SCR vehicles were usually higher than their total on-road tests because of low exhaust gas temperatures

The gasoline-full-HEV equipped with a PFI engine and non-heated TWC had substantially lower NO_x emission than the TWC-equipped G-DI vehicle. The average emission factors

for on-road tests were 0.04 (s.d. 0.02) and 5.00 (s.d. 1.29) times Euro 6 limits for HEV and GDI vehicles, respectively. In urban driving, the emission factors of HEV and GDI vehicles averaged 0.03 (s.d. 0.03) and 4.92 (s.d. 1.25) times Euro 6 limits, respectively. The large differences in emission levels of both vehicles are explained by the different powertrains and injection approaches, primarily related to air-fuel ratio control, and possibly by a defect in the NO_x control system of the GDI vehicle. The conclusion corresponds only for the tested vehicle.

Hypothesis 1.2

Cold start NO_x emission levels from Euro-6b vehicle technologies depend on the fuel and aftertreatment technologies.

Yes, cold-start (first 5 min) NO_x emission levels were more dependent on the combination of fuel type and aftertreatment because gasoline vehicles had TWC systems and diesel different technologies; see Section 4.4. TWC and SCR systems, both continuous catalytic converters, require a minimum operating temperature to light-off, which is critical to their optimal performance. For cold start, the NO_x levels were similar for each fuel type. Therefore, there were large differences between the cold start and hot-start emission levels of HEV and diesel SCR vehicles. The G-DI and HEV vehicles averaged 1.4 and 1.1 (s.d. 0.31) times Euro 6 emission limits, respectively. The diesel vehicles presented comparable emission levels, averaging 2.7 (s.d. 0.63), 2.0 (s.d. 1.24), and 3.3 (s.d. 2.39) times Euro 6 emission limits for SCR, LNT, and EGR-only (without catalytic aftertreatment) vehicles, respectively.

Research question 2

What are the impact and characteristics of the high NO_x emissions from real driving?

This study demonstrated that the high NO_x emissions occurred in particular conditions that significantly impacted the total emissions of a real driving test or phase. Further, a new methodology was developed, called high emissions sets (HES), which was used to investigate the NO_x emission peaks, their contribution to total emissions and their relationships with the vehicle, engine, and aftertreatment operation conditions. This research question is explained in-depth by the following hypothesis.

Hypothesis 2.1

The high instantaneous NO_x emissions have low occurrence and represent a high amount of total NO_x emissions from real-world tests.

Yes, this study showed that the datasets with the highest NO_x emissions (HES) are composed of few observations with NO_x emission peaks. They represent a large amount of cumulated emissions and are produced in a small amount of driving time. The theoretical constraint of the NO_x emission peaks significantly decreases distance-specific emission factors; however, because of their low occurrence, NO_x emissions must be diminished in the entire range of operating conditions to achieve Euro 6 or posterior real-world limits. This analysis was focused on diesel vehicles; see Sections 5.1 and 6.2.

Hypothesis 2.2

The high instantaneous NO_x emissions are related to vehicle, engine and aftertreatment operating conditions

Yes, the high NO_x emissions were characterised using the following variables

- a) Vehicle operating conditions: speed, acceleration, speed times positive acceleration ($v \cdot a^+$), and road grade
- b) Engine and aftertreatment: exhaust gas temperature and air-fuel ratio.

These variables were also defined as (i) externally observable variables (EOVs) and (ii) internally observable variables (IOVs), see Figure 3.1.

Power

Power demand, defined as VSP (EOV) or engine power (IOV), has a high correlation with engine-out emissions and in to a less extent with tailpipe emissions. Therefore, tailpipe emissions primarily depend on NO_x control systems and their operating conditions. In principle, higher engine-out NO_x emissions are expected in motorway sections compared with urban sections; see Section 6.4.

Speed times positive acceleration ($v \cdot a^+$) - EOVS

VSP is closely correlated to acceleration and $v \cdot a$. Regarding diesel vehicles, driving conditions with $v \cdot a^+ > 9.2 \text{ m}^2 \text{ s}^{-3}$ (NEDC limit) showed a strong potential to generate HES observations. For worse-NO_x-reducers (EGR and LNT) vehicles, the conditions of elevated vehicle speed with hard acceleration (high $v \cdot a^+$) produced high NO_x emissions, particularly in rural and motorway sections. On the other hand, the relatively high NO_x emissions of SCR vehicle (tested in Madrid) were related to high $v \cdot a^+$ values; however, they matched with conditions of hard acceleration at low vehicle speed, particularly in urban driving, see Section 5.3.2.

Speed - EOVS

Regarding driving zones, HESs are mainly generated in one modal speed value for each urban, rural and motorway sections. These speed modes mainly depend on road speed limits or RDE regulation. However, EGR and LNT vehicles were more likely to emit high instantaneous NO_x as the speed increases, particularly in motorway driving. For the SCR vehicle, this pattern is not clear because their urban driving emissions resulted in higher values compared to the total RDE emissions because of low exhaust gas temperatures. This suggests that hot spots in these operating conditions can be identified and tackled by NO_x control systems and anti-pollution policies; see Section 5.3.1.

Road grade - EOVS

During the uphill, the high engine loads increase the probability of high NO_x emissions. Long downhill showed the potential to cooldown SCR systems, which reduces the NO_x

conversion efficiency during the strong posterior accelerations; see Sections 5.3.4 and 6.3.

IOVs are detailed in the following hypothesis.

Hypothesis 2.3

Air-fuel ratio and exhaust gas temperatures, both IOVs, have a strong influence on the NO_x emission from gasoline and diesel vehicles.

Yes, this study demonstrated that air-fuel ratio is an important variable that strongly affects engine-out NO_x emissions and the performance of TWC aftertreatments. For gasoline and diesel vehicles, most of the high tailpipe NO_x emissions were observed in slightly lean mixture conditions ($1 \lesssim \lambda \lesssim 1.5$); see Sections 4.5.2 and 5.3.3.

Also, as shown in Chapter 6, low exhaust temperatures influenced the performance of the SCR tested vehicles (Madrid and Graz). Low load in urban and congested driving, constant motoring (e.g., during long downhill), and long engine-off periods worsen temperature operating conditions for aftertreatments in the case of SCR systems and in the TWC aftertreatments of HEVs.

Regarding the tested gasoline vehicles, the vehicle with a DI engine frequently operated in lean-burn conditions, while the PFI engine of the HEV frequently operates in rich conditions, particularly in urban and rural driving. Because NO_x reduction in TWCs is favoured in rich or stoichiometric conditions, the recurrent leaner air-fuel ratios of the G-DI vehicle diminished the efficiency of its TWC aftertreatment. In terms of the powertrain, the HEV tends to a fuel economy strategy; therefore, the ICE operated at high power, which led to the rich air-fuel ratios with the relative reduction in engine-out NO_x emissions and better conditions to the NO_x reduction for the TWC; see Sections 4.5 and 4.6

Hypothesis 2.4

The efficiency of SCR systems efficiency depends on working temperatures, which influences the release of NO_x emission peaks.

Yes, the real-world performance of the SCR system (tested in Graz) was strongly dependent on the working temperatures; see Section 6.5. It was found that high tailpipe emissions are the resultant of two possible situations (a) the highest engine-out emissions with a high, but not optimal deNO_x level of the SCR system and (b) not-so-high engine-out NO_x emissions with a particular or exceptional low deNO_x conditions of the SCR system. The NO_x conversion was favoured in a temperature window for the SCR-inlet gas temperature between 220–340 °C. Below or above that temperature window, the deNO_x becomes more dependent on the mass flow, with a lower conversion for higher mass flow. It is important to note that low temperatures were typical of urban driving, while high temperatures were typical of motorway driving. The low SCR-inlet temperatures not only reduce the SCR performance but can also lead to the inhibition of ammonia injection for SCR-inlet < 180 °C. Using 200 °C as the reference level, the cooling down of the SCR device is maintained during acceleration, where high power produces

high engine-out NO_x emissions. These results are explained by the unsynchronised change in the temperature between the engine-out level and the SCR-inlet level, and it supports the need for active heating to improve the performance in real-world conditions.

Research question 3

How does high NO_x emission observations impact the accuracy of microscopic NO_x predictions?

This study demonstrates that high NO_x emissions affect the prediction accuracy of microscopic models. Further, the tailpipe NO_x emissions are not only influenced by engine operating conditions but are also influenced by the aftertreatment working conditions. This research question is answered in the following hypothesis; see Chapter 7.

Hypothesis 3.1

A hybrid approach for microscopic NO_x prediction improves the accuracy of its parts: a physics-based model and a machine learning algorithm.

Yes, this study performed a comparison between different model approaches (a) based on the driving dynamics and vehicle modelling (PHEM), (b) based on EOVs and random forest (EOV-ML), and (c) based on PHEM for the prediction of engine-out NO_x emissions and a posterior use of random forest to predict tailpipe emission (Hybrid).

The results showed that the Hybrid model outperformed EOV-ML and PHEM NO_x predictions. In addition, the data-driven model reduced the challenging work of aftertreatment dimensioning, characterisation and simulation of the aftertreatment layout of the SCR-equipped vehicle. The main disadvantage of the data-driven model is the lower interpretability with respect to physics-based models. The selection of an applicable model for a determined objective in the environmental research and policy decision requires considering aspects such as interpretability, the capability to link to meso and macro models, the ability to represent a fleet of vehicles, simplicity, computational effort, ability to perform offline training, size of the model, amount and availability of the input data, among other particular characteristics required for a given application or philosophy to scale the microscopic results to higher spatial resolutions.

Hypothesis 3.2

NO_x emission peaks influence the total and instantaneous prediction error of microscopic emission models.

Yes, the correct prediction of the NO_x peaks provides a better EF error due to their low occurrence but a high impact in the total emissions or emission factors. However, it is important to achieve accuracy in the prediction of “low” emission levels because these conditions affect instantaneous error metrics such as RMSE and R².

Owing to the complexity of the new aftertreatments and powertrains, this study shows the importance to model and analyse NO_x emissions from SCR vehicles (at microscopic

level) with two blocks: (1) for the engine-out emissions (NO_x emitter), dependent of power demand; (2) for the SCR system (deNO_x device). Further, it applies to hybrid electric vehicles because of the complex management of the powertrain and the variable operating conditions of the aftertreatment; see Section 6.4.

8.2. Main contributions

The main contributions that can be extracted from this work are listed below.

- The development of a new methodology to analyse the high NO_x emissions using clustering by high emission sets (HESs)
- The determination of the impacts of NO_x peaks on emission factors, and the estimation of the emission factors considering the constraints of the NO_x emission peaks.
- The rationale to classify variables that represent vehicle, engine and aftertreatment operating conditions, and their influence on NO_x emissions. In addition, the relationship of these variables with driving aggressivity. Finally, the rationale to use these variables as IOVs and EOVs, which is useful for the selection of predictors for emission modelling.
- The correlations found between NO_x emission peaks with EOVI/IOV variables or operating conditions. Further, the use of conditional probabilities shows the probability of high instantaneous NO_x emissions removing the influence of the frequency of the analysed variables under common operating conditions.
- The detailed analysis of the SCR device efficiency in real world conditions. The results corroborated past laboratory tests that showed the dependence of deNO_x on exhaust gas flow out of the working thermal window.
- The study evidenced the relationship between NO_x emission peaks with power, driving mode and SCR-inlet temperature. Also, this demonstrates the need of active heating to improve SCR efficiency.
- The development of a hybrid model that combines a physics driven model (PHEM) and a data-driven model (random forests). The model had good accuracy and combines the strengths of both approaches.

8.3. Dissemination of results

Scientific articles

- Mera, Z., Fonseca, N., López, J.-M., Casanova, J. (2019). Analysis of the high instantaneous NO_x emissions from Euro 6 diesel passenger cars under real driving conditions. *Appl. Energy* 242, 1074–1089. <https://doi.org/10.1016/j.apenergy.2019.03.120>
- Mera, Z., Fonseca, N., Casanova, J., López, J.-M. (under review). Influence of exhaust gas temperature and air-fuel ratio on NO_x aftertreatment performance of five large passenger cars.
- Mera, Z., Claus, M., Hausberger, S., Fonseca, N. (under review). Selective catalytic reduction (SCR) system performance of a diesel passenger car in real-world conditions.

Congress proceedings

- Mera, Z., Fonseca, N., Casanova, J., López, J.M. (2019). Exhaust gas temperature and NO_x after-treatment performance of Euro 6 passenger cars, in: 23rd Transport and Air Pollution Conference - TAP2019. Thessaloniki, Greece. Retrieved from: <https://www.tapconference.org/>
- Mera, Z., Fonseca, N., López, J. M., & Grijalva, E. (2018). Estudio de episodios de altas emisiones de NO_x de un vehículo diésel Euro 6 en tráfico real, in: XXII Congreso Nacional de Ingeniería Mecánica - CNIM 2018 (pp. 717–726). Madrid, Spain. Retrieved from: <http://www.asoc-aeim.es/anales.html>
- Grijalva, E., López, J. M., Mera, Z., Marcos, D., & Resino, D. (2018). Estimación energética de una instalación solar fotovoltaica ubicada en Madrid para carga de vehículos eléctricos a partir del ciclo de conducción WLTC, in: XXII Congreso Nacional de Ingeniería Mecánica - CNIM 2018 (pp. 803–810). Madrid, Spain. Retrieved from: <http://www.asoc-aeim.es/anales.html>

Scientific posters

- García, A., Fonseca, N., Mira, J., & Mera, Z. (2019). Modelling urban bus fleet emissions with machine learning boosting methods : City of Madrid. in: 23rd Transport and Air Pollution Conference - TAP2019 (Poster). Thessaloniki, Greece.

Press release

- Universidad Politécnica de Madrid (February 2020). *¿Cuándo se producen las mayores emisiones de NO_x en los vehículos diésel?* (Press release). Retrieved from: https://www.upm.es/?id=eb5dc1dd8ae10710VgnVCM100000009c7648a____&prefmt=articulo&fmt=detail

8.4. Future works

Based on the work carried out during this thesis, new ideas for future works can be outlined for the following research areas.

NO_x emission testing

- New IT technologies allow for an increase connectivity of vehicles to the internet, and the measurement of parameters is now possible by means of OBD, data recording can be performed by Smart Emissions Measurement System (SEMS). Thus, smart NO_x sensors (as used in MIVECO) should be deeply investigated and characterised for the implementation in SEMS, and in particular, cross sensitivity with other gases must be analysed.
- RDE imposes boundary testing conditions, and outside those boundaries, the emission NO_x control strategies and devices can reduce efficiency or fail. This investigation demonstrates the effect of emission peaks on total emissions. Therefore, more investigations of real-world NO_x emissions outside RDE conditions are necessary using onboard measurement systems.

Characterization of NO_x emission peaks

- The analysis of NO_x emission peaks of post-Euro 6b passenger cars are suggested. Post-Euro 6b vehicles are designed to pass a more stringent type approval process than Euro 6b vehicles, and the behaviour of emission NO_x control systems and devices should be different.
- Future investigations can involve the prediction of NO_x emission peaks and the improvement of heating strategies for the SCR devices. Because active heating increases fuel consumption, the best trade-off between CO₂ penalty and NO_x reduction benefit must be analysed for real-world driving.

NO_x emission modelling

- A comprehensive analysis of the accuracy of machine learning algorithms for the prediction of instantaneous NO_x emissions is required. The model comparison and feature selection require extensive work because every vehicle and testing set to become an individual model.
- It is necessary to model NO_x emissions during the cold start. . The combination of physics and machine-learning models could be a powerful tool to overcome the complex phenomena involved in the cold-start NO_x emissions.
- Other area of interest is the evaluation of traffic flows to develop machine-learning models that will permit the improvement of emission inventories and models at meso- and macro-levels.

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Annexes

Annex A. Comparison of testes RDE tests and regulation

Table A1. Madrid tests

Parameters	RDE regulation COMMISSION REGULATION (EU) 2017/1151, COMMISSION REGULATION (EU) 2017/1154	Fulfil	RDE trips of this study
A. Route requirements			
Altitude	Moderate: $h \leq 700$ meters above sea level Extended: $700 < h \leq 1300$ meters above sea level	✓	Study conducted between 519 – 675 meters above sea level
	The proportional cumulative positive altitude gain over the entire trip and over the urban part of the trip shall be less than 1 200 m/100 km	✓	Proportional cumulative positive altitude gain for urban is 754m/100km
		✓	Proportional cumulative positive altitude gain for the entire trip is 828m/100km
	The start and the end point shall not differ in their elevation above sea level by more than 100 m.	✓	Start and end point differ in their elevation by 8 m
Zone distances	34 %, 33 %, and 33 % with a ± 10 % tolerance (urban shares must be major than 29 %)	✓	Average percentage share for each section is 30.3 % urban, 37.7 % rural and 32.0 % motorway
	The minimum distance of each operation: urban, rural and motorway, shall be 16 km	✓	Distance of each section is 23.2 km urban, 28.8 km rural and 24.5 km motorway
Route speed limits	Urban $\leq 60 \text{ km h}^{-1}$	✓	Madrid urban speed limit is 50 km h^{-1}
B. Verification of overall trip dynamics			
Data pre-processing	If vehicle speed is used to determine parameters like acceleration, the product of speed and positive acceleration, or RPA, the speed signal shall have an accuracy of 0,1 % above 3 km/h and a sampling frequency of 1 Hz.	✓	Speed recorded to 3 decimal places
		✗	Sampling frequency of 10 Hz
	Resolution of acceleration, $a_{res} \leq 0,01 \text{ m/s}^2$	✓	$a_{res} \leq 0,01 \text{ m s}^{-2}$
Binning of the results	Urban $0 \leq 60 \text{ km h}^{-1}$ Rural $> 60 \leq 90 \text{ km h}^{-1}$ Motorway $> 90 \text{ km h}^{-1}$	✓	sections classified only for verification of overall trip dynamics
	The number of datasets with acceleration values $a_i > 0,1 \text{ m/s}^2$ shall be bigger or equal to 150 in each speed bin	✓	At 10 Hz, the number of datasets is bigger or equal to 1500 in each speed bin
Verification of overall trip dynamics	Verification of v_{*apos_95} per speed bin	✗	Only one test slightly surpass v_{*apos_95} limit
	Verification of RPA per speed bin	✓	

C. Test requirements			
Test time	RDE tests conducted on normal workdays and hours	✓	Tests conducted in normal workdays at 9h00 (9), 11h00 (4), 14h00 (1)
Vehicle payload and test mass	Up to 90 % of the allowed payload (including driver, a witness of the test, if applicable, the test equipment with the mounting and the power supply devices); artificial payload may be added	✓	Mass of driver, witness of the test and overall equipment is about 190 kg. It represents about 60–70 % of the 'mass of the passengers'
Vehicle temperature conditions	Vehicle conditioning for cold engine-start testing	✓	Hot start was analysed without conditioning the vehicle, but with a warm engine. The vehicle covered a warm up route of 4.9 km for about 14 min. The motor temperature exceeded 70 °C in this route
	Cold start is the period from the first start of the combustion engine until the point when the combustion engine has run cumulatively for 5 min. If the coolant temperature is determined, the cold start period ends once the coolant has reached 343 K (70 °C) for the first time	✓	
Ambient temperature conditions	Moderate: $0 \leq T \leq 30$ Extended (low): $-7 \leq T < 0$ Extended (high): $30 < T \leq 35$	✓	Study temperature between 13.0 – 32.6 °C. Six tests had some observations over 30 °C
Trip duration	The trip duration shall be between 90 and 120 minutes	✓	Trips duration 95 – 112 min
Urban driving	The average speed of the urban driving part of the trip should be between 15 and 40 km h ⁻¹ .	✓	Study average speed of urban section 20.1 – 25.6 km h ⁻¹ .
	Stop periods, defined as vehicle speed of less than 1 km h ⁻¹ , shall account for 6–30 % of the time duration of urban operation.	✗	Study average stop periods 21.3 – 34.7 % of urban time. Three tests have more than 30 % of stop periods
	Urban operation shall contain several stop periods of 10 s or longer	✓	Study contained stop periods of more than 10s.
	Individual stop periods shall not exceed 300 consecutive seconds; else the trip shall be voided	✓	Study has no stop period more than 300 s.
Motorway Speed	The speed range of the motorway driving shall properly cover a range between 90 and at least 110 km h ⁻¹	✓	Study average speed of motorway section 104 km/h, average maximum 129 km h ⁻¹
	The vehicle's velocity shall be above 100 km h ⁻¹ for at least 5 minutes	✓	Study time above 100 km h ⁻¹ in motorway section 8.0 – 10.1 min
	Vehicle velocity shall normally not exceed 145 km h ⁻¹	✓	Speed does not exceed 145km h ⁻¹ . Absolute maximum 135.4 km h ⁻¹
Classification of urban/ rural/ motorway	Urban $0 \leq v \leq 60$ km h ⁻¹ Rural $60 < v \leq 90$ km h ⁻¹ Motorway $v > 90$ km h ⁻¹	✗	Sections classified using GPS

(Binning of results)			
D. Trip dynamic conditions and emissions			
Verification of trip dynamic conditions	Method 1 (Moving Averaging Window) Method 2 (Power Binning)	X	Raw distance–specific emissions computed
RDE emissions	Method 1 (Moving Averaging Window) Method 2 (Power Binning)	X	Raw distance–specific emissions computed

Table A2. Graz tests

Parameters	RDE regulation Commission Regulation (EU) 2017/1151, Commission Regulation (EU) 2017/1154	Fulfil	RDE trips of this study
A. Route requirements			
Altitude	Moderate: $h \leq 700$ meters above sea level Extended: $700 < h \leq 1300$ meters above sea level	✓	Study conducted between 312 – 576 meters above sea level
	The proportional cumulative positive altitude gain over the entire trip and over the urban part of the trip shall be less than 1 200 m/100 km	✓	Proportional cumulative positive altitude gain for urban is 1039–1093m/100km
		✓	Proportional cumulative positive altitude gain for entire trip is 860–881m/100km
	The start and the end point shall not differ in their elevation above sea level by more than 100 m.	✓	Start and end point differ in their elevation by 1–4 m
Zone distances	34 %, 33 %, and 33 % with a ± 10 % tolerance (urban shares must be greater than 29 %)	✓	Average percentage share for each section is 32–34 % urban, 33–35 % rural and 33–34 % motorway
	The minimum distance of each operation: urban, rural and motorway, shall be 16 km	✓	Distance of each section is 27–29 km urban, 28–30 km rural and 28–29 km motorway
Route speed limits	Urban ≤ 60 km h ⁻¹	✓	Graz urban speed limit is 30 or 50 km h ⁻¹
B. Verification of overall trip dynamics			
Data pre-processing	If vehicle speed is used to determine parameters like acceleration, the product of speed and positive acceleration, or RPA, the speed signal shall have an accuracy of 0,1 % above 3 km/h and a sampling frequency of 1 Hz.	✓	Speed recorded to 3 decimal places
		✓	Sampling frequency of 1 Hz
	Resolution of acceleration, ares $\leq 0,01$ m/s ²	✓	ares $\leq 0,01$ m s ⁻²
Binning of the results	Urban 0 to ≤ 60 km h ⁻¹ Rural > 60 to ≤ 90 km h ⁻¹ Motorway > 90 km h ⁻¹	✓	
	The number of datasets with acceleration values $a_i > 0,1$ m s ⁻² shall be bigger or equal to 150 in each speed bin	✓	At 10 Hz, the number of datasets are bigger or equal to 150 in each speed bin
Verification of overall trip dynamics	Verification of $v_{\text{apos}}[95]$ per speed bin	✓	All sections are below limits
	Verification of RPA per speed bin	✓	All sections are above limits
C. Test requirements			
Test time	RDE tests conducted on normal workdays and hours	✓	
Vehicle payload and test mass	Up to 90 % of the allowed payload (including driver, a witness of the test, if applicable, the test equipment with the mounting and the power supply devices); artificial payload may be added	✓	Mass of driver, witness of the test and overall equipment was about 234 kg. It represents about 40 % of the ‘mass of the passengers’
	Vehicle conditioning for cold engine–start testing	✓	

Vehicle temperature conditions	Cold start is the period from the first start of the combustion engine until the point when the combustion engine has run cumulatively for 5 min. If the coolant temperature is determined, the cold start period ends once the coolant has reached 343 K (70 °C) for the first time	–	Cold start was not analysed
Ambient temperature conditions	Moderate: $0 \leq T \leq 30$ Extended (low): $-7 \leq T < 0$ Extended (high): $30 < T \leq 35$	✓	Study temperature between 14 – 22 °C.
Trip duration	The trip duration shall be between 90 and 120 min	✓	Trips duration 106 – 111 min
Urban driving	The average speed of the urban driving part of the trip should be between 15 and 40 km h ⁻¹	✓	Study average speed of urban section 25.3 – 26.1 km h ⁻¹
	Stop periods, defined as vehicle speed of less than 1 km h ⁻¹ , shall account for 6–30 % of the time duration of urban operation.	✓	Study stop periods 24 – 30 % of urban time
	Urban operation shall contain several stop periods of 10 s or longer	✓	Study contained stop periods of more than 10s.
	Individual stop periods shall not exceed 300 consecutive seconds; else the trip shall be voided	✓	Study has no stop period more than 300 s.
Motorway Speed	The speed range of the motorway driving shall properly cover a range between 90 and at least 110 km h ⁻¹	✓	
	The vehicle's velocity shall be above 100 km h ⁻¹ for at least 5 minutes	✓	Study time above 100 km/h in motorway section 13 – 14 min
	Vehicle velocity shall normally not exceed 145 km h ⁻¹	✓	Speed does not exceed 145 km h ⁻¹ Maximum 134 km h ⁻¹
Classification of urban/ rural/ motorway (Binning of results)	Urban $0 \leq \leq 60$ km h ⁻¹ Rural $> 60 \leq 90$ km h ⁻¹ Motorway > 90 km h ⁻¹	✓	
D. Trip dynamic conditions and emissions			
Verification of trip dynamic conditions	Method 1 (Moving Averaging Window) Method 2 (Power Binning)	✗	Raw distance–specific emissions computed
RDE emissions	Method 1 (Moving Averaging Window) Method 2 (Power Binning)	✗	Raw distance–specific emissions computed

Annex B.

HES times and thresholds for the diesel-SCR vehicle tested in Graz

Table B1. HES times and thresholds for the diesel-SCR vehicle (Graz)

HES	Time [%]	NO _x threshold [mg s ⁻¹]
0	0.0 (s.d. 0.00)	69.0 (s.d. 2.41)
10	0.3 (s.d. 0.04)	45.3 (s.d. 6.51)
20	0.6 (s.d. 0.08)	34.4 (s.d. 4.46)
30	1.1 (s.d. 0.15)	27.7 (s.d. 5.70)
40	1.7 (s.d. 0.26)	21.4 (s.d. 5.24)
50	2.5 (s.d. 0.44)	16.8 (s.d. 4.64)
60	3.6 (s.d. 0.76)	11.4 (s.d. 4.19)
70	5.4 (s.d. 1.28)	6.8 (s.d. 2.99)
80	8.7 (s.d. 2.19)	3.4 (s.d. 1.53)
90	16.4 (s.d. 3.87)	1.1 (s.d. 0.39)
100	100.0 (s.d. 0.00)	0.0 (s.d. 0.00)

The table presents average values