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Exhaust emissions of ammonia from spark ignition engines fitted with three-way catalytic converters under transient operating conditions

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Abbreviations and symbols used

$\frown$	upstream notation (i.e. upstream of an emissions control device)
λ	lambda; the relative air:fuel ratio
CH_4	methane
CI	compression ignition
CO	carbon monoxide
CO_2	carbon dioxide
$DeNO_x$	process leading to the conversion of NO_x to other chemical species
EPA	Environmental Protection Agency
EU	European Union
FTIR	Fourier transform infra-red (spectroscopy)
FTP-75	US Federal test procedure commonly known by that name
H_2	hydrogen
H_2O	water
HD	heavy-duty
HCN	hydrogen cyanate
HNCO	isocyanic acid
HONO	nitrous acid
IR	infra-red
LD	light-duty
{RNC}	proportion of the summed concentration of all considered RNC occurring in the form of a given RNC, e.g. {NH_3}
NH_3	ammonia
N_2O	nitrous oxide
NEDC	New European Driving Cycle
NO	nitrogen monoxide
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen ($NO + NO_2$)
OSC	oxygen storage capacity
PEMS	portable emissions measurement system
QCL	quantum cascade laser
RDE	real driving emissions
RNC	reactive nitrogen compound(s) i.e. $NO + NO_2 + NH_3 + N_2O$
SO_2	sulphur dioxide
SO_3	sulphur trioxide
SO_x	oxides of sulphur ($SO_2 + SO_3$)
SR	steam reforming
THC	total hydrocarbons
T50	light-off temperature; the temperature at which TWC conversion effectiveness reaches a value of 50% for the first time
T90	the temperature at which TWC conversion effectiveness reaches a value of 90% for the first time
TWC	three-way catalytic converter
WGS	water-gas shift
WHTC	World Harmonized Transient Cycle
WLTC	Worldwide Harmonized Light Vehicles Test Cycle
WLTP	Worldwide Harmonized Light Vehicles Test Procedure

Abstract

The subject of this thesis is the phenomenon of the presence of ammonia (NH_3) in the exhaust gas emitted from vehicular powertrains of road vehicles featuring spark ignition (SI) internal combustion engines (ICEs) and three-way catalytic converter (TWC) exhaust gas aftertreatment.

Ammonia's place within the spectrum of harmful compounds present in exhaust gas is examined and particular attention is paid to the relationship between emissions of NH_3 and NO_x. Examinations of formation mechanisms and various controlling factors are made and attempts are made to bridge the gaps between the relatively plentiful investigations on the subject present in the literature, which span some five decades.

The measurement of NH_3 concentrations (and gravimetric emissions) are discussed, within the context of testing performed in the automotive sector. Measurement challenges and their mitigation are identified and discussed.

A range of experimental work conducted under laboratory conditions is reported. Experiments were performed to characterise NH_3 emissions from a pool of light-duty (LD) vehicles with SI engines of varying technical characteristics, carried out over multiple driving cycles. This is followed by more detailed investigations into a sub-set of vehicles selected on the basis of their emissions results and powertrain characteristics. Results obtained from experiments involving modified test procedures are presented. Furthermore, results from testing of a single heavy-duty (HD) SI engine running on natural gas are presented, in the context of analysing current European Union (EU) technical requirements for type approval of such powertrains and further analysis of the relationship between emissions of NH_3 and NO_x, as well as aged TWC aftertreatment.

Experimental findings are discussed in detail, with frequent reference to existing literature; special attention is paid to the examination of the proportion of reactive nitrogen in the exhaust gas which occurs in the form of NH_3, as well as thermal effects and cold start effects and their impact on NH_3 emissions. Powertrain operation parameters not associated with significant NH_3 emissions are identified and attempts are made to link emissions to the fundamental chemical effects identified in the literature review.

The existing legal requirements (and lack thereof) regarding NH_3 in vehicular exhaust gas are discussed and critiqued. Experimental results obtained in the work reported are analysed in the context of a potential emissions limit for the species NH_3. Potential precedents and approaches for deriving a gravimetric NH_3 emissions limit for LD vehicles are discussed and justifications are made for the introduction of an NH_3 emissions limit, together with discussions of the practicalities and implementation of such a limit.

Emisja amoniaku w spalinach silników o zapłonie iskrowym wyposażonych w trójfunkcyjne reaktory katalityczne w dynamicznych warunkach eksploatacji

Streszczenie

Przedmiotem pracy jest zjawisko obecności amoniaku (NH_3) w spalinach emitowanych z układów wylotowych pojazdów drogowych wyposażonych w silniki spalinowe o zapłonie iskrowym (ZI) oraz w trójfunkcyjne reaktory katalityczne (ang. TWC).

Pierwsze doniesienia na temat obecności NH_3 w spalinach silników ZI pojawiły się w literaturze naukowej już około pięćdziesiąt lat temu. Pomimo że NH_3 jest naturalnym składnikiem atmosfery, gaz ten uważany jest za szkodliwy. W większości badań i raportów z ostatnich lat stwierdzono, że emisja NH_3 z pojazdów z silnikami ZI ma duże znaczenie dla środowiska, w szczególności dla jakości powietrza w miastach.

W pracy omówiono znaczenie amoniaku wśród szkodliwych związków obecnych w spalinach, ze szczególnym uwzględnieniem relacji pomiędzy emisją NH_3 i emisją tlenków azotu (NO_x). Przeprowadzono analizę mechanizmów powstawania NH_3 w TWC oraz analizę czynników mających na to wpływ. Praca podejmuje również próbę wypełnienia luk w literaturze na ten temat. Omówiono zasady pomiaru NH_3 w kontekście motoryzacyjnym, wraz ze specyficznymi zjawiskami i utrudnieniami pomiaru, wynikającymi z właściwości cząsteczki NH_3.

W dysertacji przedstawiono wyniki badań eksperymentalnych przeprowadzonych w warunkach laboratoryjnych. Badania wstępne obejmowały pomiary emisji NH_3 z floty pojazdów lekkich (LD) z silnikami ZI, przeprowadzonych w różnych cyklach jezdnych. Następnie przeprowadzono bardziej szczegółowe badania zbioru pojazdów, wybranych na podstawie ich wyników emisji NH_3 i charakterystyki układu napędowego. Zaprezentowano także wyniki uzyskane z eksperymentów, w których zastosowano zmodyfikowane przez autora procedury badawcze. Ponadto przedstawiono wyniki badań silnika ZI typu *heavy-duty* (HD) zasilanego gazem ziemnym, uwzględniając aktualne wymagania techniczne Unii Europejskiej (UE) dotyczące homologacji tego typu układów napędowych. Końcowa część pracy dotyczy określenia zależności pomiędzy emisją NH_3 i NO_x oraz starzeniem się (deaktywacją) reaktora TWC.

Wyniki wykonanych badań omówiono w pracy odwołując się także do innych prac dostępnych w literaturze. Szczególną uwagę zwrócono na badania udziału azotu reaktywnego (ang. *reactive nitrogen compounds, RNCs*) w spalinach, który występuje w postaci NH_3, a także efektów termicznych oraz efektów wynikających z zimnego rozruchu oraz ich wpływu na emisję NH_3. Wykazano, że skład mieszanki palnej (współczynnik λ) jest bardzo istotny w kontekście powstawania NH_3, ponieważ wartość tego parametru określa ilościowo dostępność wodoru (H_2, który może reagować z NO_x, tworząc NH_3), a także tlenku węgla (CO, który może brać udział w reakcjach tworząc wodór i który jest ściśle związany z tworzeniem NH_3), a także tlenu (O_2, który inhibituje powstawanie NH_3 w TWC). Kolejnym czynnikiem o dużym znaczeniu jest temperatura TWC. Stwierdzono, że w temperaturze reaktora zapewniającej sprawną konwersję NO_x, zachodzi również znaczna emisja NH_3.

Wykonane badania i analizy pozwoliły na wyciągnięcie wniosków, które można podsumować w następujący sposób:

- Zimny rozruch został zidentyfikowany jako główny czynnik przyczyniający się do emisji NH_3 z nowoczesnych pojazdów z silnikami ZI. Profil emisji NH_3 niektórych pojazdów jest zdominowany przez tę fazę pracy silnika, przynajmniej w powszechnie stosowanych cyklach badawczych, takich jak WLTC.

- Stwierdzono, że cykle jezdne o dynamicznym profilu prędkości powodują intensywniejsze powstawanie NH_3. Jednak efekt ten nie zawsze przekłada się na wzrost jednostkowej emisji NH_3, ze względu na wpływ odległości pokonywanej przez pojazd podczas cyklu.
- Niektóre pojazdy (w tym hybrydowe) wykazują mały poziom NH_3 w szerokim zakresie warunków jazdy – rzędu kilku mgNH_3/km. Częste uruchamianie silnika w pojazdach z hybrydowymi układami napędowymi jest istotną przyczyną powstawania NH_3. Wydaje się jednak, że jest to z nadwyżką kompensowane przez okresy, w których silnik spalinowy nie pracuje, a więc NH_3 w ogóle nie powstaje.
- Niektóre pojazdy charakteryzują się dużymi emisjami, wykazując podwyższone stężenie NH_3 w spalinach w bardzo szerokim zakresie warunków pracy układu napędowego. Nawet po stabilizacji termicznej oraz podczas pracy na biegu jałowym. Przyczyna tego nie jest w pełni jasna, ale przypuszczalnie wynika raczej z właściwości TWC zamontowanych w takich pojazdach, niż z właściwości samego silnika lub strategii sterowania układem napędowym.
- Warunki podczas tzw. „odcięcia paliwa" (brak zasilania) powodują bardzo szybki i silny spadek stężeń NH_3 (a więc także grawimetrycznej emisji NH_3). Takim zdarzeniom zazwyczaj towarzyszy mierzalna fala NO_x w spalinach, co oznacza, że chwilowy udział NH_3 wśród RNC w spalinach spada do małego poziomu, aż do czasu wznowienia powstawania NH_3.
- Specyfika przebiegu prędkości pojazdu w momencie aktywacji TWC (w szczególności T50 dla NO) wydaje się mieć znaczący wpływ na zachowanie emisji NH_3 i może zauważalnie ją zwiększać. W tym kontekście duże znaczenie ma także tzw. efekt crescendo.
- Cykle jezdne z bardzo małym obciążeniem mogą prowadzić do zmniejszenia emisji NH_3, co jest zgodne z innymi wnioskami dotyczącymi wpływu λ i natężenia przepływu paliwa. Istnieją dowody na efekt „płukania", w którym wcześniej utworzony NH_3 pozostaje w układzie wylotowym (w tym w skroplonej tam wodzie) przez pewien czas i uwalnia się gdy moc wyjściowa silnika wzrasta. Ten „utajony" NH_3 może być istotnym czynnikiem podczas badania w szczególności pojazdów hybrydowych.
- Analizy składu spalin podczas przyspieszania pojazdów, wykazały, że emisje RNC są zdominowane albo przez NH_3, albo przez NO_x (który składa się prawie wyłącznie z NO).
- Starzenie się układu oczyszczania spalin prowadzi do zwiększonej emisji NO_x poprzez zmniejszenie efektywności konwersji NO_x obecnych w spalinach, ale wynikający z tego wpływ na emisję NH_3 jest bardziej złożony. Wykonane badania nie wykazały jednoznacznego związku między starzeniem się TWC i emisją NH_3, Podobnie nie zaobserwowano korelacji pomiędzy emisją NH_3 a przebiegiem badanego pojazdu, mimo, że takie powiązania były niekiedy raportowane w literaturze.
- Badane pojazdy wykazywały typowe emisje NH_3 w porównaniu z innymi badaniami opublikowanymi w ostatniej dekadzie. Badania własne potwierdziły, że nowoczesne pojazdy charakteryzują się emisją NH_3 rzędu 20 mg/km.

Tendencja do tworzenia NH_3 w TWC jest silnie kontrolowana przez czynniki, które mogą zmieniać się w bardzo krótkich okresach czasu (tj. punkt pracy silnika – λ, temperatura, stężenie NO, H_2 oraz CO), jak również te, które zmieniają się w dłuższych okresach (zmiany w naturalnej selektywności wynikające ze stopniowych procesów fizykochemicznych w TWC lub zdolność układu napędowego do utrzymywania ścisłej kontroli λ). Istnieją także zmienne, które są stałymi parametrami, takimi jak konstrukcja/specyfikacja TWC, temperatura typowych cyklów pomiarowych i specyfikacje paliw. W przypadku danego pojazdu na danym etapie przebiegu, zakres stężeń i emisji grawimetrycznych NH_3 jest warunkowany punktem pracy układu napędowego, temperaturą i składem chemicznym TWC, które rozpatrywane całościowo i wspólnie, dostarczają ogólnie zadowalających wyjaśnień dla częściowo rozbieżnych wyników emisji NH_3 wskazywanych w literaturze.

1. Introduction

1.1. The continuing importance of exhaust emissions and their quantification and control

Internal combustion engines (ICEs) are widely used in a wide range of applications and contexts, most notably in road transport. Despite the existence of other powertrain types, including compression ignition (CI) and indeed purely electrical powertrains, on a global scale, the clear majority of smaller road vehicles (passenger cars and smaller vans, often together referred to as LD (LD) vehicles) feature spark ignition (SI) engines as their only (or primary) means of propulsion. The majority of HD (HD) road vehicles feature CI powertrains, but non-negligible numbers of such vehicles are in use. The total number of such vehicles and the high spatiotemporal density at which they are used in urban environments and along key inter-urban routes means that exhaust emissions occurring as a result of SI powertrain operation are of considerable importance, from multiple points of view.

The vast majority of LD vehicles equipped with combustion engines (generally speaking, all passenger cars, small vans, light trucks, etc, along with motorcycles, and – in many markets – all but the smallest scooters, quads and trikes) are subject to legislation aiming to limit their exhaust emissions. The topic has a long history, which, at the time of writing, spans almost six decades – see [1], [2], [3], [4] for detailed accounts. While considerable progress has been made in terms of quantifying, limiting and reducing harmful emissions from vehicles with SI ICEs, the topic remains the subject of great technical and political interest. Indeed, in the current era in which electric vehicles (EVs) – which do not produce any in-use tailpipe emissions – are gaining market share among new vehicles, the case for appropriate limitation of harmful emissions from vehicles with ICEs is clear. Modern vehicles with SI ICEs emit harmful exhaust gas components at far lower levels than their predecessors. However, the philosophies of “BAT – best available technology” and “ALARP – as low as reasonably practicable”, as well as improved understanding of the depth and range of impacts caused by certain harmful emissions, affecting both human health and the environment itself, force ongoing reassessment of the maximum level of such emissions which can be considered both acceptable and technically achievable. While the phrase “zero [exhaust] emissions” has come into favour in recent years, such a concept is not achievable for any vehicle with an ICE and a far more pertinent question is “how close to zero do harmful exhaust emissions need to be?” It must, however, be recalled that exhaust gas is a complex mixture of chemicals in the gaseous state, in highly variable proportions. The setting of emissions limits targeting species known to be harmful therefore requires identification of key species of concern deemed worthy of limitation. This decision, as to whether a certain compound should be limited, has important implications for the vehicle development cycle, affecting the process that leads from a vehicle type being first designed to being approved for sale. For species known to have deleterious impacts, which are also known to be present in exhaust gas, but for which there is no legal requirement to perform measurements, nor a legally binding emissions limit to be met, questions will inevitably be raised as to whether that compound should become subject to legislative (and technical) control.

Control of any type of exhaust emission species requires a detailed understanding of its origin, as well as the chemical nature of the species. Such knowledge permits both evaluation of the best strategies and approaches for quantification of the species, leading to detailed understanding of emissions phenomena and ultimately to strategies to limit emissions to a level which as a bare minimum meets legal requirements (i.e. does not exceed the applicable emissions limit). Owing to the complex chemical nature of exhaust gas and well-known effects resulting from manipulation of the wide array of variables for SI engines, it is widely recognised that efforts to control and limit the emission of one harmful species can affect the magnitude and behaviour of other species, a situation which raises obvious questions over the effectiveness of the emissions control measures (both technical and legal).

It is in the aforementioned context that this thesis and all work contained herein is presented.

1.2. The issue of exhaust emissions of ammonia from modern vehicular powertrain systems

While not a widely appreciated or generally well-known fact, the presence of NH_3 in the exhaust gas of SI powertrains is well attested to in the literature, appearing in a range of publications spanning around five decades. As Heeb et al. [5] stated in 2011:

> *"It is not common knowledge that ammonia emissions have already been tolerated for gasoline-, CNG-, and LPG-vehicles equipped with TWCs".*

As is reflected the above quotation – and indeed in the title of this thesis, a crucial caveat to note is the fact that NH_3 is present in noteworthy quantities only in the case of powertrains fitted with three-way catalytic converters serving as exhaust gas aftertreatment. That is to say, NH_3 is not formed in significant quantities in the combustion reaction occurring within the cylinder(s) of the ICE. As is explored in detail in following sections of this thesis, the mechanism of formation is via catalytically-facilitated reactions occurring within the exhaust gas aftertreatment system. Here it is important to distinguish between combustion-based *sources* and the combustion *event* itself – an example of the former being the powertrain fitted to a passenger car and an example of the latter being the combustion event occurring within the engine of that car. It is also important to clearly distinguish the case of the release of unreacted ammonia ("NH_3 slip") from exhaust systems selective catalytic reduction (SCR), as commonly fitted to modern vehicular powertrains based on CI engines. While the term "exhaust emissions" as commonly understood is often associated with the combustion reactions which are strictly confined to the ICE's cylinders, the formation of ammonia occurs in the aftertreatment system through reactions which have little in common with oxidation reactions, being much more properly described as reduction reactions, since the final product is NH_3, self-evidently a highly reduced form of nitrogen.

The majority of studies and reports from the past few years have concluded that NH_3 emissions from vehicles with SI engines are of notable or even high relevance in urban air quality contexts (see [6], [7], [8], [9] and references therein, as well as [10], [11] and [12]). Quantitative rigour has been given to such assertions by the use of isotopic tracing signatures which can point towards the likely origin of NH_3 molecules in ambient air – often resulting in the identification of vehicular emissions as a significant source [13], [14], although vehicles with CI engines (with SCR) are also mentioned in this context. Such views, which constitute the majority opinion amongst researchers in various countries and active in diverse fields, are not universal, as some authors find the contribution of vehicles to be negligible [15], [16], or to be significant but consistently decreasing [17]; that is to say, lower for more recent model year vehicles meeting more stringent emissions standards (e.g. [18]). Individual EU member states do not show consistent data when considering long-term trends in NH_3 emissions [19] and changes in NH_3 emissions trends such as agriculture and industry might obscure (or even cancel out) changes in emissions from the road transport sector. Even within the road transport sector, changes to aftertreatment systems used in vehicles with CI powertrains (both light and HD) have an impact on NH_3 emissions behaviour and complicate direct analysis of tendencies and trends and assessment from only a few years ago may no longer be fully valid, due to the shifting vehicle powertrain landscape. An assessment by the European Environment Agency found that NH_3 emissions attribute to road transport had increased by 336% over the period 1990-2011 [20]. Given that TWCs were in limited use in the EU in 1990 and that NH_3-based SCR systems were not nearly as common in the road transport sector in 2010-2011 as they are now, this would appears to firmly implicate TWCs as the primary source of the increased NH_3 emissions from the road transport sector, but such points require regular re-evaluation, in light of potential changes in levels of TWC-facilitated NH_3 emissions, and the prevalence of NH_3-based SCR systems.

Of the total annual NH_3 emissions in the entire territory of the EU, a mere 1% is thought to originate from road transport [19], although the aforementioned effects relating to sources in urban areas should be recalled here, as well as possible changes occurring since publication of the cited study. The conclusions of studies of the magnitude and relevance of NH_3 originating from road transport (see [21] for a recent example) – whether laboratory-based, or whether making use of data from remote sensing or investigations of ambient concentrations and various attempts at source apportionment – are unlikely to be universal in nature and may be directly contradicted by other studies.

Complex interactions between legislative, financial and technical requirements have guided research and development on exhaust gas aftertreatment systems since the inception of such technology. It is important to remember that the technical and economic incentive for the development of TWCs was to enable vehicle manufacturers to sell their vehicles in jurisdictions which had set limits for exhaust emissions. As such, the final chemical configuration in which the exhaust gas exited the TWC was not necessarily of particular technical interest, nor of direct economic importance, aside from the fact that the proportion of the gas in the forms subject to legislative limits had to be sufficiently low so as to make the TWC an attractive component for vehicle manufacturers to specify in their designs, rather than attempting to rely on other measures, or indeed the catalytic emissions control products offered by competing suppliers. Attempts at using solutions not based on the TWC concept proved futile in the face of the stringent emissions requirements introduced in the USA in the 1970s and TWCs were adopted by the industry with relative alacrity, spreading to other markets and remaining in use to this day.

The reduction of oxides of nitrogen (NO_x) within a TWC is an eminently complex, non-trivial process consisting of multiple steps; much early research on TWCs and their functionality was only able to describe processes and phenomena empirically. The *potential* for the chemical conversion of NO_x to lead to the creation of chemical species other than the harmless idealised target species (N_2) is an inescapable fact for such a system. Selectivity towards N_2 as the final product would appear to be the obvious goal, but as will be shown, this cannot always be assumed. It is well recognised that the demands placed on an aftertreatment system are very complex and under certain circumstances such demands conflict to a degree; the highly variable operating conditions demanded of and encountered by ICEs used in road transport applications (particularly passenger cars) leads to a colossal number of permutations and thus a very wide range of overall physicochemical conditions to which the TWC will be subjected during normal use. If a small subset of these combinations cause significant ammonia emissions, the resulting final quantities of ammonia emitted during a given duty cycle will, to a reasonably high degree of confidence, simply consist of a function of the frequency with which the aforementioned conditions occur during the duty cycle under consideration.

1.3. Ammonia and its role as an anthropogenic environmental pollutant

Ammonia, chemical formula NH_3, also given the systematic names trihydridonitrogen or nitrogen trihydride, is the smallest and simplest pnictogen hydride, and a relatively well-known inorganic compound. Normally encountered in the gaseous phase (boiling point: –33.3°C (239.8 K)), its relatively low density (around 40% lower than that of air) gives it reasonably high mobility. The molecule features a lone pair of electrons and the significant difference in electronegativity between hydrogen and nitrogen mean that the molecular structure exhibits polarity; both these facts have important implications for its chemical behaviour and indeed implications for its quantification in gas analysers. Ammonia is widely recognised as exhibiting high reactivity and high solubility and it is described as hydrophilic, sometimes even strongly hydrophilic. Ammonia's odour is distinct, characteristic and considered to be thoroughly disagreeable, caustic and sharp, bringing to mind desiccated urine. The odour is unfortunately perceivable by the human nose at concentrations as low as a few parts per million (ppm) [22], [23], although the limit of perception varies between individuals and may sometimes be as low as 1.5 ppm [10]. The gas is completely colourless at any concentration. Ammonia is flammable and can be explosive under certain conditions, but such characteristics do not pose hazards where concentrations are low, as in the case of NH_3 pollution in ambient air.

Ammonia and associated compounds have been recognised as potent, potentially harmful chemicals since antiquity [24]. While it is known as an unpleasant substance best avoided, its status a toxic pollutant able to affect human health and the broader environment is less well known. Ammonia is a naturally occurring chemical of great importance in many biological and geochemical processes and the only major basic gaseous component of the Earth's atmosphere. Despite this status as a chemical widely encountered throughout the biosphere, NH_3 is considered a pollutant, often mentioned as being toxic, corrosive, and generally detrimental to the environment [25], [26].

Concentrations of ammonia in ambient air vary considerably around the world and often exhibit high seasonality. Many areas have no significant sources of NH_3 (neither natural nor anthropogenic) and at such locations the atmospheric mixing ratio at ground level is normally extremely low: < 1 part per billion (ppb). Other areas containing sources of NH_3 emission have higher ambient levels, on the order of 1 ppb for weakly affected sites, up to 10–12 ppb for strongly affected sites [10]. These levels reflect the background concentration at relatively large scales; within the close vicinity of a source (or sources) of ammonia, the local concentration can be significantly higher. There is abundant evidence that ambient concentrations of ammonia have increased greatly over the past century or so [27], [28], [29]. Notwithstanding the wide range of natural and agricultural sources of NH_3, quantitative evidence shows that ammonia concentrations can be high in areas with little or no agricultural activity (and, in fact, at times NH_3 concentrations in such areas are even higher than in rural areas where ambient ammonia can be directly apportioned to agriculture) [30], [31], [32].

Assessments show that in recent decades in the EU overall emissions of ammonia have remained stable or undergone only modest changes, but that the modality – the relative contribution of the range of sources – has shifted significantly [20]. However, NH_3 budget uncertainties are considerable, in part because of the fact that quantification of gaseous NH_3 concentrations – in many contexts – is challenging to perform in a reliable, repeatable, representative and technically rigorous fashion [27]. Measurements are often subject to considerable variation and measurement errors [33], [34], [35], [36], although these problems should be expected to decrease in severity – at least somewhat – higher NH_3 concentrations (e.g. for the ppm range compared to the ppb range) [37]. Accurate measurements of NH_3 concentrations present technical challenges applicable to many fields, but quantification of NH_3 in a static body of ambient air represents a very different case from measurement of its concentration in a fast-moving stream of exhaust gas which contains many other pollutant species in rapidly varying proportions, as well as significant quantities of water vapour.

Over the past several decades, the interaction of ammonia with other gaseous species and the formation of pollutants including suspended fine particulate matter has been the subject of significant research efforts in the area of atmospheric (and specifically aerosol) science and air quality investigations [11], [38], [39]. Despite the availability of detailed, recent literature on the subject and the fact that almost all comprehensive analyses of air quality mention NH_3, ammonia pollution is widely regarded as a topic that is somewhat neglected [29], [40] – or at least underestimated [41], with varying sources of NH_3 underestimated to various degrees [42]. In the EU, NH_3 is monitored and analysed in ongoing evaluations of anthropogenic emissions and air quality, but NH_3 is not included as a pollutant in the air quality standards for the protection of health established in various EU directives [43]. The aforementioned list of pollutants includes PM_{10} and $PM_{2.5}$, which include secondary particulate [43] –

thus, it could be argued that NH_3 participating in the formation of secondary PM is indirectly monitored and thereby made subject to targets and limits. The Gothenburg Protocol on trans-boundary air pollution [44], [45] includes NH_3 as one of the main pollutants within its scope, but the scope as pertains to NH_3 is mainly restricted to agricultural sources.

The impact of ammonia and ammonia-based compounds on water quality and aquatic ecosystems has also come into focus as an anthropogenic environmental problem of note [43], [46], [47]. The presence of oxides of nitrogen and sulphur oxides (SO_x; i.e. SO_2 and SO_3) in air can allow the formation of nitric and sulphuric acid, which then react with ammonia; the end products of such a reaction chain are the aerosol species ammonium nitrate and ammonium sulphate [48], [49], [50], [51]. Such aerosols are termed secondary particulate matter (secondary PM – as such particulate is not emitted into the atmosphere in that form, but formed within that medium through gas-gas reactions, as outlined above). Ammonia has been identified as one of the main atmospheric precursors of $PM_{2.5}$ and a key promotor for the formation and growth of secondary inorganic aerosols [11], [52], [53], [54], [55]. In many real-world situations NH_3 is the limiting reagent for formation of secondary fine particulate [51], [53], [56], [57]. A study considering the impact of NH_3-based secondary PM found that the mass of particulate formed via that mechanism had the potential to significantly exceed the primary PM emitted from the vehicle’s exhaust [58]. In addition to oft-noted interactions between NH_3 and NO_x (including primary NO_2 originating from road transport) [59], a study found that NH_3 showed a strong tendency to interact with evaporative emissions from petrol-fuelled vehicles, the result of which was formation of noteworthy quantities of secondary PM [60].

Generally speaking, ammonia-based aerosols have significantly longer atmospheric lifetimes than NH_3 itself [61]. Concern over anthropogenic ammonia emissions forms an important part of analyses of human-induced perturbations in the global nitrogen cycle and as such the topic is closely linked to oft-expressed concerns over humanity’s impact on that cycle and associated sustainability considerations [6], [23], [40], [62], [63], [64], [65], [66].

The aforementioned points above have led to the creation of legal measures to control emissions of NH_3 and thereby limit the deleterious impacts of gaseous NH_3 of anthropological origin. The most recent EU legislation to control general emissions of various pollutants [67], which is closely based on the Gothenburg Protocol [45], focuses closely on ammonia emissions, but with a near-exclusive focus on the agricultural sector. It has nevertheless been recognised that ammonia originating from non-agricultural sources must also be quantified, understood and ultimately controlled and limited [68], in order to obtain a holistic picture of the entire network of flows in the context of the nitrogen cycle. This is especially important for urban environments of high population density, where there is no agriculture, little vegetation and often little heavy industry, but where road traffic powered by ICEs is currently omnipresent [69], [70].

1.4. Ammonia as a reactive nitrogen compound in the automotive context as the subject of this thesis

While the main subject of this thesis is ammonia (NH_3), frequent reference will also be made to other reactive nitrogen compounds (RNCs). Fuels commonly used in SI ICEs do not contain appreciable amounts of nitrogen. Thus, the nitrogen atoms entering the cylinder do so in the form of the diatomic nitrogen present in ambient air, with the general addition of any other forms of nitrogen which happen to be present in the ambient air (at extremely low levels in comparison to N_2). Such traces present in ambient air can include including other vehicles’ RNC emissions. The result of this is that the mixture taken in by the engine can be considered to contain significant amounts of nitrogen in only one form: diatomic N_2. The triple bond which occurs in this diatomic molecule is well known for its high strength – indeed, N_2 is renowned for its stability as a molecule and its inert nature, which changes only at very high temperatures (such as encountered in a flame front). This high stability means that despite the high temperatures (~2800 K) and pressures (routinely in excess of 30 bar) occurring within an SI engine during its working (Otto) cycle, the vast majority of nitrogen exits the engine in the same form as it entered, namely as N_2. Nitrogen emissions from engines are very rarely subject to measurements, since the gas is merely the main component of ambient air; the "non-RNC" nitrogenous component can be assumed to be N_2. Table 1 shows basic some key data on the four species normally termed RNCs.

Table 1. Basic physicochemical characteristics of the four species given the appellation reactive nitrogen compounds

Compound formula	Molecular weight (to two decimal places) [Da]	Mass relative to lowest mass RNC (NH_3)	N atom count	O atom count	H atom count	N:O ratio	N:H ratio	H:O ratio
NO_2	46.01	2.70	1	2	0	1:2	–	0
NO	30.01	1.76	1	1	0	1:1	–	0
N_2O	44.01	2.58	2	1	0	2:1	–	0
NH_3	17.03	–	1	0	3	–	1:3	–

RNCs in the exhaust gas emitted from combustion engines first came into focus via the well-known and intensively-studied topic of the formation of NO_x in SI engines – see, inter alia, [71], [72], [73], [74], [75] for detailed discussions. Further candidates for inclusion in the RNC category could potentially include isocyanic acid (HNCO), nitrous acid (HONO) and, as well as various cyanates, including hydrogen cyanate (HCN), yet these compounds are rarely studied in the automotive context and will not be included in the RNC definition adopted here; see [50], [76], [77] and [78] for detailed discussions of emissions of this type.

The reason for the consideration of compounds other than NH_3 as an integral part of discussions focusing on NH_3 itself will become apparent in further sections. The best known RNCs are subjected to scrutiny, but those emissions themselves are emphatically not the main focus of this work. Nevertheless, a key argument of this thesis relates to the relevance of the continuum of RNCs to vehicular exhaust emissions control – since NO_x forms an inalienable part of that continuum, its frequent mention is thus fully warranted. The essential fact remains that the exhaust gas produced by an SI engine, prior to passing through the aftertreatment system, essentially only one RNC is present at significant concentrations – NO_x. Despite the definition of NO_x consisting of both NO and NO_2, levels of the latter are low enough that they may be neglected in many contexts, i.e. $NO \approx NO_x$. Thus, considering the aftertreatment (three-way catalyst (TWC)), the input of a single RNC (NO) can lead to the output of multiple RNCs: NH_3, N_2O, even other compounds such as HCN [79], HCNO [50] and HONO [80]. In addition, since the conversion effectiveness of the TWC is finite, unreacted NO_x is also present, at highly variable levels. The fact that all of the aforementioned compounds except NO_x are not formed in significant quantities within the ICE itself is of great relevance, as the overall environmental performance of a TWC must be balanced in terms of the harmful emissions it eliminates and harmful emissions it creates. As this thesis tracks, for decades TWCs have been deployed and viewed as one of the main keys to improving the environmental performance of vehicles with SI engines [81], with eminent and widely-praised advantages, but arguably without fully adequate consideration of their *disadvantages*. While the technical issues have long been known, this has neither translated into legislative action to tackle the problem, nor into any formal requirements for demonstration of the limited scale of the problem.

1.5. The RNC proportion analysis concept

A summation of the concentrations of the four individual RNCs (or at least those which have been measured) is a simple yet effective measure of the instantaneous RNC flux from a source such as an engine. The concentrations of the individual RNCs can then be compared to this RNC sum to determine the normalised contribution of each species to the total RNC flux. Here the notation {RNC} will be used to denote the dimensionless proportion of the RNC under consideration in the molar balance. In the case of ammonia, $\{NH_3\}$:

$$\{\mathrm{NH_3}\} = \frac{[\mathrm{NH3}]}{\Sigma\,[\mathrm{NO}][\mathrm{NO_2}][\mathrm{NH_3}][\mathrm{N_2O}]} \qquad (1)$$

where [RNC] is the volumetric concentration of each individual RNC measured and {RNC} is the volumetric concentration of the RNC (or RNCs) of interest. Note that this concept can be applied to measurements taken from any point on the powertrain, i.e. both upstream and downstream of a TWC, or indeed in ambient air.

Summation of the instantaneous gravimetric (mass) flows, or total masses emitted over a given period of observation of two or more RNCs produces a result of lower relevance, since the variable densities of the four species (ranging by a factor of significantly more than two) cause a poor correlation between mass flows and the number of moles (and thus molecules). As NO as a species is regulated (via NO_x limits) and is converted to other chemical forms within modern TWCs at high efficiencies for the majority of engine operating conditions, and since selectivity towards N_2 is generally finite and in fact considerably lower than idealised, even relatively low concentrations of NH_3 can account for the majority of the RNCs measured in the exhaust – that is to say, $\{NH_3\}$ as defined in (1) can take very high values for the majority of a driving cycle, as long as the post-TWC concentration of NO remains low. Examples of such calculations, their physical significance and their utility in examining RNC emissions behaviour are explored in later sections of this thesis.

Since N_2 is emphatically not an RNC, the RNC concentration is not necessarily conserved within a gas stream. For example, when passing through a TWC, it is common for the concentration of NO_x to fall significantly and the concentration of NH_3 and N_2O to rise, yet the magnitude of the fall in the NO_x concentration is normally greater than the increase in the concentration of NH_3 and N_2O. In such an example, the total RNC concentration has not been conserved as the gas stream passed through the TWC. Due to the varying densities of the RNCs, more favourable comparisons of RNC concentrations can be obtained using molar concentrations, rather than gravimetric emissions rates ([mg/s], [g/s]). However, in terms of comparisons to legislative emissions of regulated compounds (especially NO_x), gravimetric units are significantly more insightful – with distance-specific units for passenger cars [g/km, mg/km] and work-specific units used for HD vehicles and engines [g/kWh, mg/kWh].

Considering the nitrogenous species N_2 and the four RNCs (as defined above), both upstream (denoted with the symbol $\frown$) and downstream, the overall balance takes the following form:

$$\widehat{N_2}/2 + \widehat{NO} + \widehat{NO_2} + \widehat{NH_3} + \widehat{N_2O}/2 = N_2/2 + NO + NO_2 + NH_3 + N_2O/2 \quad (2)$$

In most cases, NH_3 and N_2O need not be measured upstream of the TWC and post-TWC measurement provides sufficient data to perform an RNC balance. Since N_2 is present on both sides at very high levels (and since nitrogen is very rarely measured in automotive contexts), the implied change in its molar concentration ∂N_2 can be considered instead:

$$\widehat{NO} + \widehat{NO_2} = NO + NO_2 + NH_3 + N_2O/2 + \partial N_2/2 \quad (3)$$

For further simplicity, or where data are lacking, the sum of $NO+NO_2$ may be denoted by NO_x.

$$\widehat{NO}_x = NO_x + NH_3 + N_2O/2 + \partial N_2/2 \quad (4)$$

From the purely legislative point of view, at the time of writing, in most contexts[1], the only exhaust gas RNC component worthy of optimisation is NO_x; from the holistic, least harm-inspired emissions control point of view, the RNC species NH_3 and N_2O must also be minimised and consequently $\frac{\partial N2}{2}$ must be maximised, since unfixed nitrogen is the only major unreactive product.

This balance can be re-arranged to isolate $\frac{\partial N2}{2}$. If the concentration of N_2O is known, then the RNC balance is compete (5a), or, where not known, it can be approximated (5b):

$$\widehat{NO}_x - \left(NO_x + NH_3 + N_2O/2\right) = \partial N_2/2 \quad (5a)$$

$$\widehat{NO}_x - (NO_x + NH_3) \approx \partial N_2/2 \quad (5b)$$

As $\widehat{NO}_x$ is characterised by high concentrations, often taking values within the range ~1000-3000 ppm and as NH_3 and N_2O concentrations are characterised by numbers typically up to 4 orders of magnitude lower (and which can take values indistinguishable from zero), ∂N_2 can take very high values. However, the perfect conversion of 5000 ppm of NO to N_2 would result in 2,500 ppm of N_2 (i.e. 0.25% v/v), which is clearly of very limited significance compared to the level of N_2 already present in both intake air and exhaust gas (~78% v/v).

Short-term storage (of any species) and/or apparent loss of N atoms to other species such as cyanates could be a significant confounding factor in such considerations, especially where concentrations are subject to very rapid fluctuations, as is often the case for highly transient engine operation. By design, the catalytically active surfaces of the TWC have a strong propensity to adsorb NO, that functionality being a crucial part of the mechanism that provides the so-called "DeNO$_x$" (NO$_x$ conversion) functionality. However, once formed and released from the surface of the TWC, NH_3 has the strongest tendency to undergo storage and release effects (i.e. short- to mid-term storage) when in contact with hard materials, including the types of metals used for vehicular exhaust systems. Ammonia is also more hydrophilic and reacts more readily with water than the other RNCs, generally speaking. Taking those two facts into consideration, it is clear that the fidelity of an RNC balance could be somewhat compromised by such effects, as well as measurement artefacts, especially where shorter timescales are considered.

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[1] Refer to Table 2 in section 1.6.

1.6. Regulation and control of exhaust emissions from spark ignition engines used in road transport

The fundamental approach applied to regulation of gaseous exhaust emissions from LD vehicles has converged on essentially a single strategy: to specific a maximum quantity (mass) of a specified compound which can be emitted per unit distance covered. In a limited number of cases a much simpler metric is adopted, namely limiting the concentration of a given pollutant that may be detected in the exhaust gas, yet such measures are outdated. Concentration-based limits have been replaced (or at least supplemented) by more demanding gravimetric, distance-specific emissions limits. Some conformity checks continue to stipulate that a concentration-based measurement be performed this way, but as regards current global automotive emissions legislation, the only limit applicable to vehicle operation (not idling) laid down purely in terms of concentration in fact is for ammonia emitted from certain types of engine (a topic which will be returned to later). Self-evidently, any measurement made while the vehicle is not moving cannot be expressed in in distance-specific terms; any mass-based limit is dependent on the sampling time, since mass flow accumulates.

Starting with some historical perspective, as an example, in the USA the EPA mandated ambitious emissions limits in 1975. These limits effectively forced the use of a catalytic emissions control system. In further developments, the emissions limit was progressively lowered and a NO_x emissions limit was introduced, as shown in Figure 1 – note the $\log_{10}$ vertical axis, attesting to reductions of approximately 2 orders of magnitude over a period approaching 30 years.

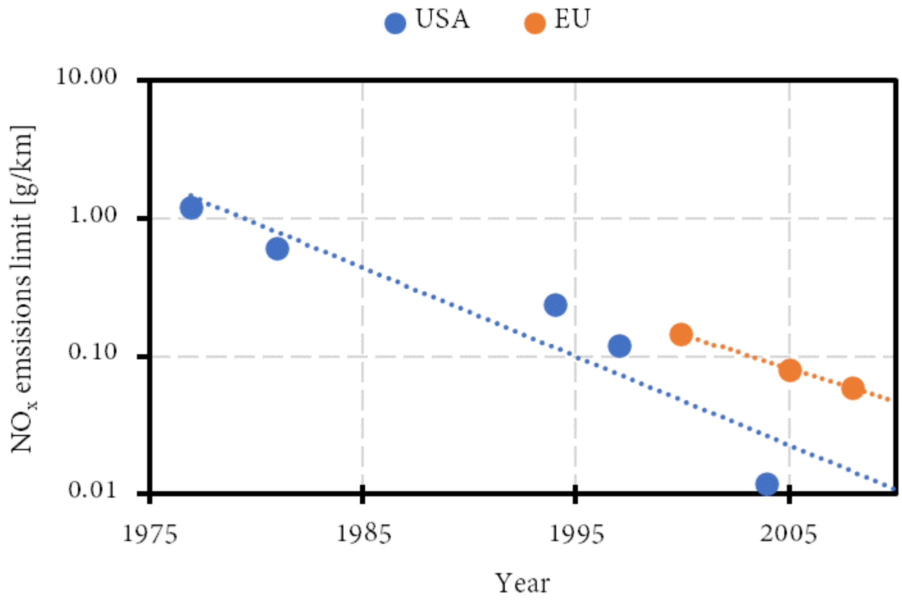

Figure 1. Historical evolution of NO_x emissions limits applied to LD vehicles in the USA and the EU; note that in the case of the EU, the limits shown are those that apply to vehicles with SI engines

Noting the $\log_{10}$ vertical axis, the vast reduction in the magnitude of the limits is immediately apparent. Note that the NO_x limit decreased by just over an order of magnitude in twenty-four years (1975-99). Since the early 2000s, the US authorities have continued to mandate lower emissions limits. Certain details have been changed and additional limits have been added, yet the onward trend to lower emissions has continued unabated. Figures 2 and 3 show the evolution of emissions limits for light-duty vehicles with SI engines in the EU.

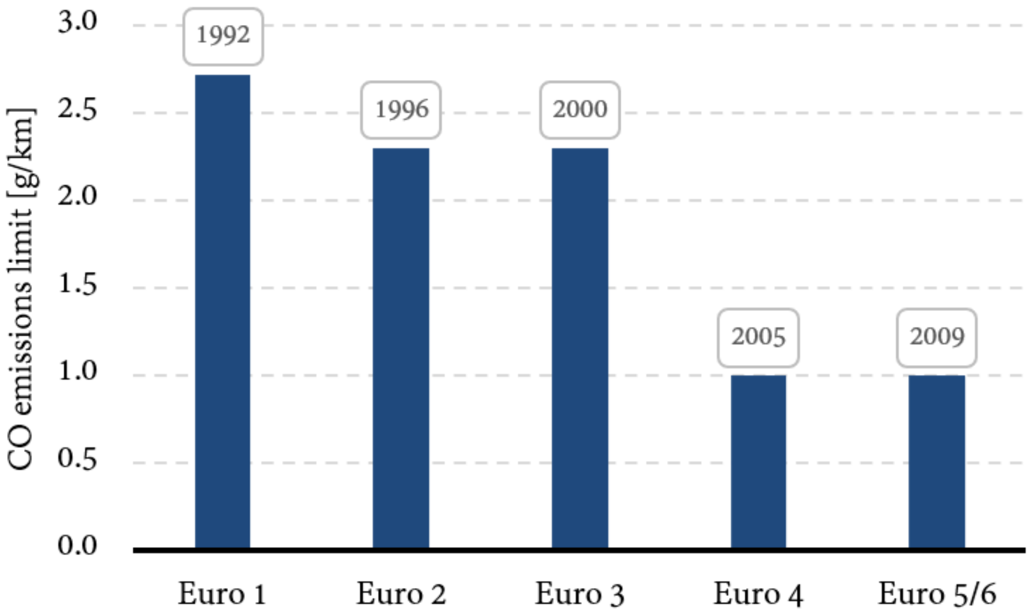

Figure 2. Emissions limits for the regulated pollutant carbon monoxide (CO), applicable to LD vehicles with SI engines, as set by and applied within the EU and its legal predecessors; the year in which each limit became applicable to new vehicles is shown

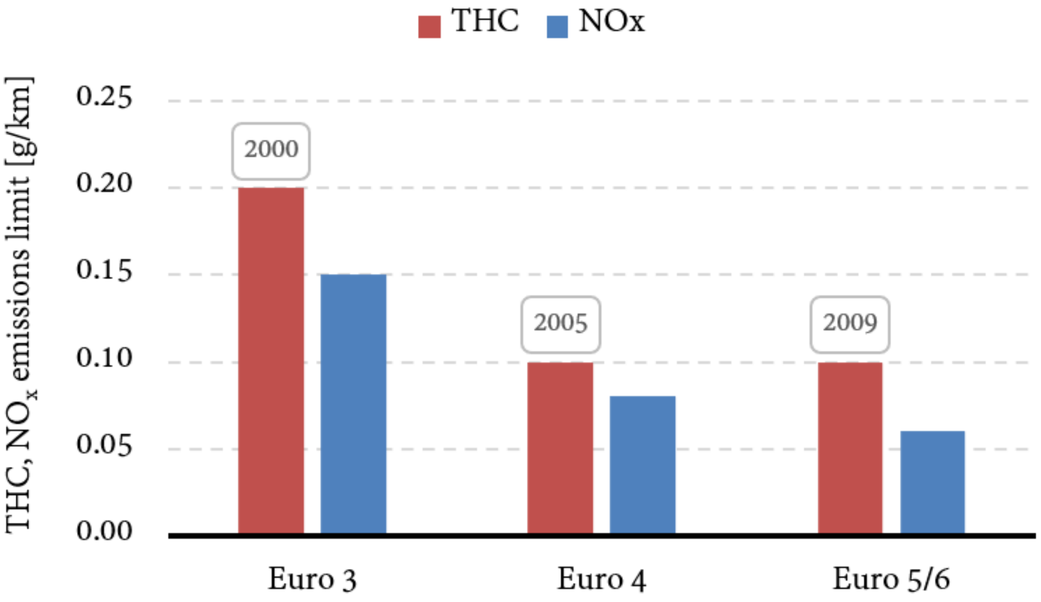

Figure 3. Emissions limits for the regulated pollutants total hydrocarbons (THC) and NO$_x$, applicable to LD vehicles with SI engines, as set by and applied within the EU and its legal predecessors; the year in which each limit became applicable to new vehicles is shown

The smallest commercial vehicles equipped with SI engines are subject to the same limits as passenger cars, while larger commercial vehicles with SI engines have their own, somewhat higher limits. HD vehicles are subject to work-specific (rather than distance-specific) emissions limits in all major markets. In the USA, a more complex fleet average approach is used, meaning there is no single NO$_x$ limit for all LD vehicles.

Overall, the situation in many other jurisdictions is similar to the situation in the EU, whereby absolute limits are set for certain pollutants. While other legal authorities started to regulate exhaust emissions significantly later than in the USA, the overall trend of requiring progressively lower emissions has played out around the globe in the various markets that have such legislative requirements. A basic comparison of international exhaust emissions norms from 2014 onwards is presented in Figure 4.

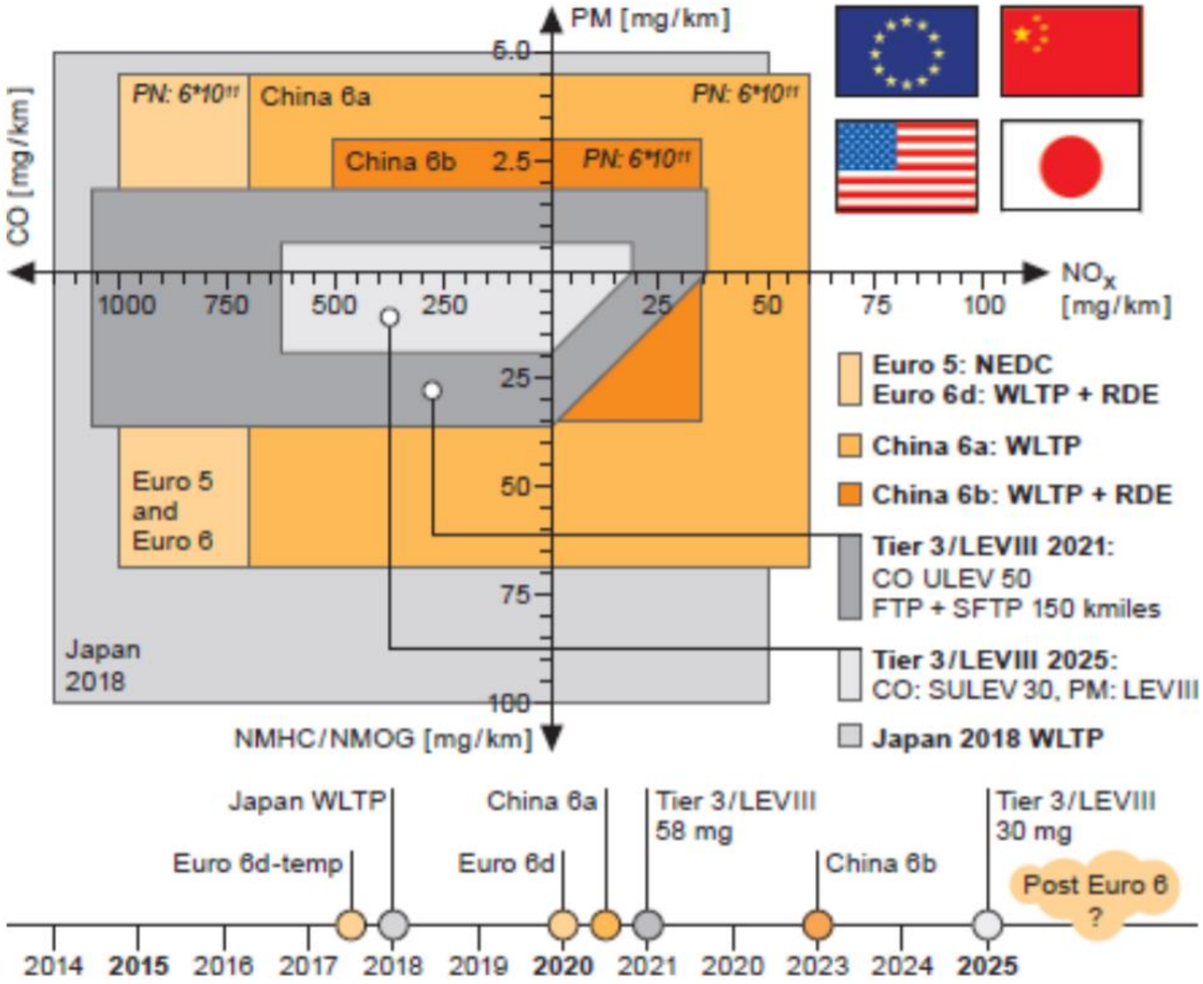

Figure 4. Comparison of international exhaust emissions standards for light-duty vehicles with SI engines, from 2014 onwards; image source: [82]

In the EU, the NO_x emissions limit for passenger cars with SI engines Euro at the Euro 5 (2009) and Euro 6 (2014) levels is the same: 60 mg/km and this is the limit in force at the time of writing; however, a further emissions standard, until recently known as “Post-Euro 6” and now commonly referred to as “Euro 7”, is expected to be announced soon [83].

The present situation regarding regulation of exhaust emissions for the largest automotive markets is summarised in Table 2.

Table 2. Simplified comparative summary of emissions regulation strategies for light-duty vehicles sold in the main automotive markets

Jurisdiction	Fundamental approach	Low ambient temperature emissions testing	Main regulated gaseous compounds
EU	Chassis dyno test, on-road testing (RDE)*	Yes*	THC*, NMHC*, CO, NO_x*, THC+NO_x*
US EPA/CARB	Multiple chassis dyno tests, requirement that in-use emissions be "similar"	Yes	NMOG+NO_x, CO, N_2O
Japan	Chassis dyno test, on-road testing (RDE)*	No	NMHC, CO, NO_x
India	Chassis dyno test, on-road testing (RDE)*	No	THC*, NMHC*, CO, NO_x*, THC+NO_x*,
China	Chassis dyno test, on-road testing (RDE)	Yes*	THC, NMHC, CO, NO_x, N_2O
South Korea	Chassis dyno test, on-road testing (RDE)*	No	THC*, NMHC*, CO, NO_x*, THC+NO_x*
Brazil	Chassis dyno test, on-road testing (RDE)*	No	NMOG+NO_x, CO, N_2O

1.7. Focus on the regulation of RNC emissions from road vehicles

As the topic at hand is ammonia emissions, the legal situation regarding exhaust emissions of RNCs and specifically NH_3 are examined in Table 3. Here the scope is broadened to include HD vehicles.

The widespread use of NH_3 as the reagent in reactions to reduce NO_x emissions via SCR and the inevitable escape of at least some unreacted ammonia from such a system (ammonia slip) has served as inspiration for the imposition of concentration-based NH_3 emissions limits. Many instances of SCR used on much larger flue gas streams (mainly in power generation applications) are subject to ammonia slip limits, usually expressed in concentration terms (on the order of ppm – often < 10 ppm, [84]). The limits applied to automotive SCR systems are also concentration-based, for the reason mentioned above [85]. The aforementioned existing concentration-based limit represents a significant a departure from current automotive emissions control philosophies. Nevertheless, at the time of writing, this concentration-based limit is the only available direct point of comparison for a legal NH_3 limit. The extension of this limit to HD vehicles with SI engines sets an important precedent, being the only example of a legal requirement to limit the quantity of NH_3 emitted from SI powertrains used in road transport (at the time of writing).

Table 3. Simplified comparative summary of RNC emissions regulation strategies for light- and heavy-duty vehicles sold in the main automotive markets

Jurisdiction	Status of LD/HD emissions limits for RNCs other than NO_x	Status of HD NH_3 limit
EU	None	Limited; mean concentration-based limit of 10 ppm applicable to all CI and SI engines
South Korea	None	Limited; mean concentration-based limit of 10 ppm applicable to all engines fitted to vehicles exceeding 3500 kg reference mass
US EPA/CARB	N_2O limited as part of GHG legislation; no NH_3 limit	Not formally limited; recommended mean concentration-based maximum value for powertrains with SCR
China	N_2O limited as part of fuel-neutral, integrated pollutant & greenhouse gas legislation; no requirements relating to NH_3	Limited; fuel-neutral mean NH_3 concentration-based limit of 10 ppm
All other jurisdictions	No known legal provisions at the time of writing	

Given the properties of ammonia and the potential for wide-ranging deleterious impacts on both human health and the environment, measuring and limiting ammonia alongside NO_x would appear to be justifiable [86]. Such an argument is given further weight by the status of N_2O, which is currently regulated in the USA and in China. Thus, for the very large combined US and Chinese markets, NH_3 is the only RNC which is not currently regulated. In US legislation, N_2O is regulated in the context of greenhouse gas emissions (as it is a powerful and long-lived greenhouse gas [87]) with a numerically low but relatively undemanding limit of 10 mg/mile (6.2 mg/km) which merely ensures that future powertrain designs do not cause emissions to exceed current levels, since certain vehicles emit at around 1 mg/mile (i.e. 10% of the limit) [88]. The Chinese N_2O emissions limit is less demanding still at 20 mg/km, but underpinned by a similar philosophy – to ensure that future emissions control strategies do not lead to increases in emissions of N_2O. However, in addition to its high global warming potential, N_2O is also a pollutant whose harmful effects include the destruction of stratospheric ozone [87] and there is growing concern over increasing atmospheric concentrations [87].

2. Aims and scope of the work

This thesis aims to synthesize the state of the art regarding the topic and to present experimental results obtained via a detailed characterization of SI powertrains and their NH_3 emissions.

To this end, two main bodies of work are presented in this thesis:

- A review of the available technical literature, attempting to gain insight into the fundamental causes and the apportionment of various effects to the variable NH_3 emissions factors reported in the literature. The literature review is broad in nature and includes a review of historical research on the subject, with the aim of demonstrating the low technical novelty of the problem.
- A range of experimental work is presented, consisting of characterization of the NH_3 emissions from a range of modern European vehicles (and one HD powertrain) tested under laboratory conditions. This characterization included both standard and modified test procedures, attempting to gain further insight into certain effects identified in the aforementioned technical literature review.

3. A literature review into the fundamental origins of NH_3 emissions and possible causes behind their variability

3.1. An overview of key historical research

This section focuses on historical publications; more recent studies and their main conclusions are cited and reviewed in the specific context discussed in other sections.

The history of the concept of NH_3 being emitted from vehicles with spark-ignition engines dates back several decades, even to the era before TWCs were commonly fitted as standard equipment. In 1967, Harkins and Nicksic [89] noted a lack of data on NH_3 concentrations in vehicular exhaust gas and performed their own experiments to attempt to determine the level. Using a contemporary test vehicle with no reported exhaust gas aftertreatment of any kind, they measured low but detectable concentrations of ~1-6 ppm. (Such findings were broadly replicated 13 years later in a study which compared NH_3 levels from vehicles with TWCs to those without them [90].) Nevertheless, Harkins and Nicksic stated that despite the measured level of only a few ppm of NH_3, up to 10% of ambient ammonia concentrations could be attributed to vehicular emissions (presumably in coastal California, where the experiments were performed). From 1972 to 1974 Shelef and Gandhi significantly extended the state of the art on the subject with their ground-breaking detailed discussions of NH_3 formation within TWCs [91], [92], [93]. Further contributions were also made by others [94], [95], [96] writing from the perspective of fundamental catalysis phenomena. A series of publications from 1974 onwards ([96], [97], [98], [99], [100]) reported experimental findings confirming the highly complex, non-binary nature of the NO-CO-H_2 system within a TWC (see [101] for commentary) and provided detailed discussions of the role played by various cyanates in the formation of NH_3 and the reduction of NO in general. The term “unregulated emissions” came into use at around this time, a definition which often included NH_3. A note-worthy publication from 1977 with the title “Unregulated Emissions from Three-Way Catalyst Cars” [102] specifically considered the case of NO reduction in a TWC and the topic of maximisation of system selectivity towards N_2.

Studies with an applied chemistry and catalytic (surface science) focus – rather than an applied automotive focus – are significantly more likely to have included measurements of ammonia emissions and detailed consideration of nitrogen balances, since most vehicle and engine test facilities have not featured equipment for the quantification of NH_3 emissions, due to the lack of legal requirements to perform such measurements[2]. Nevertheless, some vehicle manufacturers investigated and published their findings – two key papers from 1979 [94] and 1980 [103] included NH_3 emissions in the context of comparing the impact of regulated and unregulated emissions from TWC-equipped vehicles. A study from 1979 [104] applied computer modelling to consider means of increasing the effectiveness of TWCs, including minimisation of NH_3. A study published in 1980 [90] noted very low NH_3 emissions from vehicles with SI engines without a TWC and significant NH_3 emissions from TWC-equipped SI engines. Removing the TWC (where present) was found to noticeably decrease NH_3 emissions, a finding in full agreement with all other studies (from any era) measuring pre-TWC NH_3 levels; in this context the NH_3 levels reported in [89] might be ascribed to the measurement accuracy of analysers in use in the 1960s.

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[2] This situation persists to this day, for the most part. Despite the existence of a HD NH_3 concentration limit in the EU, not all engine dynamometer test cells feature apparatus for the quantification of NH_3. In terms of chassis dynamometer test cells for vehicle testing, while some R&D facilities are equipped with analysers capable of measuring NH_3, the majority of chassis dyno facilities do not feature permanent, dedicated NH_3 analysis. This situation is similar non-EU automotive markets and jurisdictions.

Due to intensive work on TWCs in preparation for the demanding emissions requirements which were phased in during the 1970s, it can be assumed that many parties were aware of the phenomenon and probably awaited a potential increase in environmental and political interest in TWC-facilitated NH_3 emissions with considerable apprehension. Indeed, from [102] it is abundantly evident that the US EPA was well aware of at least the potential for NO_x control mechanisms to result in the formation of certain deleterious species, including NH_3. There are in fact some indications in the literature that some steps were taken to reduce selectivity to NH_3 in early TWCs [105].

Throughout the 1980s there appears to have been a relative lull, as significant publications on the subject appear in the literature less frequently than in the preceding decade, despite overall interest on the subject of exhaust emissions and aftertreatment continuing to increase, in part linked to political moves to force the adoption of TWCs in markets beyond the USA. A detailed review of materials commonly used in TWCs and the resulting chemical phenomena from 1988 [106] underlined the complexity of platinum group metal (PGM)-support interactions in terms of promotion of various reactions in the context of overall TWC functionality, noting the involvement of oxygen storage capacity (OSC) materials in various catalytic processes and mentioning the resulting impact on NH_3 formation. A 1990 publication detailing Volkswagen's work on unregulated gaseous exhaust emissions [107] presented NH_3 emissions results from a range of vehicles. Vehicles with SI engines without aftertreatment and all vehicles with CI engines showed very low NH_3 emissions levels, but vehicles with catalysed SI engines showed NH_3 emissions of up to 300 mg/mile (i.e. ~185 mg/km), depending on the vehicle in question and the vehicle operating conditions. In 1992 a thorough investigation of the mechanisms involved and factors determining the nitrogen selectivity of TWCs [108] yielded multiple important insights, and identified temperature as a key controlling parameter. The use of isotopic tracing in that study enabled detailed, quantitative investigation of reactions and adsorption/desorption phenomena.

A detailed applied catalysis study published in 1998 [109] added to existing knowledge on the subject, commenting from a viewpoint which had advanced considerably since the studies of the 1970s and 1980s. That study noted the potential for high NH_3 yields under a range of conditions and showed data showing that the selectivity towards N_2 formation (the intended purpose of a TWC as regards NO_x abatement) could take low values under certain conditions. A field study the same year [110] revealed that some vehicles emitted large quantities of NH_3 (such that the automotive contribution to ambient NH_3 in the Los Angeles area was estimated at 15%). The same study also mentioned the need to control NH_3 emissions to reduce secondary PM.

The new millennium saw the publication of several key studies on the topic. In 2000-2001 the University of California [111] and the US EPA [112] published studies detailing their highly empirical investigations into the subject conducted at the vehicle level.

Further reports from Durbin et al. [113], [114] followed, mirrored soon after in Europe by Heeb and co-authors [115]. A remote sensing study from the same era [116] revealed real-world NH_3 emissions to be broadly in line with (though overall somewhat lower than) emissions factors for LD SI vehicles from the aforementioned chassis dynamometer studies.

The studies by Durbin et al. and Heeb et al. brought to light an important point which had not figured largely in the catalytic reactor-type studies of the 1970s and had been examined (but not conclusively answered) in 1980 [90] – namely: "how should ammonia be measured in the automotive context, for experiments performed at vehicle or powertrain level?" Heeb et al. performed a study comparing multiple NH_3 measurement approaches and noted the eminent unsuitability of a constant volume sampling (CVS) system for such measurements; Durbin et al. warned against the use of dilution tunnels, for essentially the same reasons. Substantial sample delay and partial (or even total) sample loss was the chief phenomenon cited. The topic of the formation of ammonia and isocyanic acid on TWCs during the reduction of NO was examined in detail in a noteworthy applied catalyst publication from 2004 [101], reflecting increased interest in the topic of unregulated emissions. Heeb and later co-authors broadened their measurements (and indeed the range of analysis) into the field of RNCs, presenting insightful analyses into the correlation with hydrogen in the exhaust gas [117] and discussions of the proportion of RNCs emitted in the form of NH_3 [118]. A very broad yet detailed study published in 2009 [119] examined a wide range of emissions from road vehicles measured under real operating conditions, including NH_3. That study provided a concise literature review and resented data testifying to the reasonably low level of NH_3 emissions, as well as reporting correlations with other pollutant species.

3.2. Chemical origins of NH_3 emissions

A hypothetical "direct" NH_3 formation route occurring in the TWC involving reactions between diatomic nitrogen and hydrogen, i.e.

$$\mathrm{N_2 + 3H_2 \rightarrow 2NH_3} \tag{6}$$

was adjudged theoretically unlikely and experimentally proven not to occur within a TWC in 1972 [120]; in the intervening decades, this position has not been challenged in the literature and such a reaction is not considered here.

In terms of viable reactions involving fixed nitrogen, at least four main reactions purporting to represent the possible chemical pathways for TWC-facilitated NH_3 formation are commonly found in the literature.

Of these, the following two are mentioned most frequently and have the highest physical significance.

$$\mathrm{2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O} \tag{7}$$

$$\mathrm{2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2} \tag{8}$$

Note the involvement of CO in (8). The stoichiometric requirements implied by the molar coefficients suggest that below the stoichiometric NO:H_2 requirements of 2:5 for (7), the reaction will be limited by H_2 and can reasonably be considered unlikely to occur. The 2:3 NO:H_2 ratio implied by (8) is obviously lower, but (8) necessitates the involvement of another species. These critical ratios are mentioned in the literature in the context of the stoichiometric requirements presenting a barrier to significant NH_3 formation – especially the "non-CO" ratio of 5:2 (e.g. [121]). Nevertheless, it has been reported that significant NH_3 formation may be observed at NO:H_2 ratios < 2:5 [122] – and in fact even at ratios of 1:1 [123].

Despite the complex behaviour of hydrogen, the availability of free (molecular) hydrogen should be expected to control the favourability of NH_3 formation reactions. Exhaust gas H_2 content is rarely measured, but has been reported to take values >1500 ppm where the mixture is stoichiometric ($\lambda = 1$), or where there is an excess of fuel ($\lambda < 1$), as shown in Figure 5.

The molar ratio of H_2 to CO has been reported to take values of approximately 0.33 for fuel types with carbon weight fractions of 0.85, i.e. standard petrol [71][3]. Under stoichiometric – and especially fuel-rich – conditions, the non-negligible level of hydrogen present in the exhaust gas can be further supplemented by hydrogen formed by two key reactions, namely steam reforming (SR) of hydrocarbons:

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[3] Heywood [71] gives an empirical third order equation yielding proportions which always take values > 0.3, although in the same work Heywood simplifies to a static approximation of one third, i.e. 0.33.

$$C_xH_{2y} + yH_2O \rightarrow CO + (x + y)H_2 \quad (9)$$

and via water-gas shift (WGS) via CO:

$$CO + H_2O \rightarrow CO_2O + H_2 \quad (10).$$

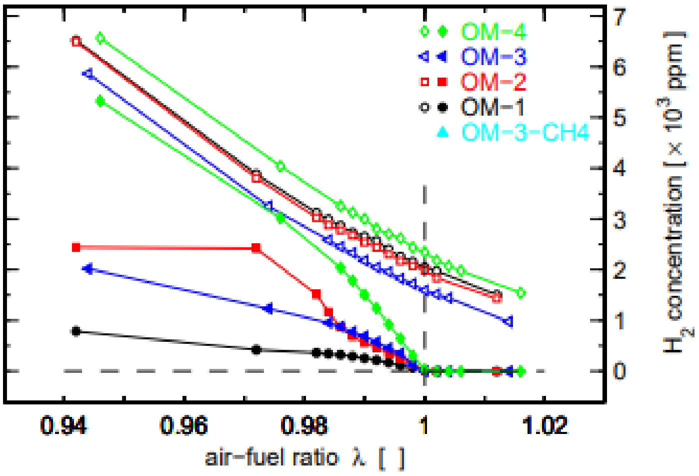


Figure 5. Exhaust as hydrogen concentration as a function of the normalised air:fuel ratio (λ). The hollow markers (top) show pre-TWC concentrations; the solid markers (bottom) show post-TWC concentrations; the dashed vertical line represents stoichiometry. Figure adapted by author; original image source: [124]

However, as has been much discussed in the literature, the likelihood of NH_3 formation reactions is controlled not only by reagent availability and the stoichiometric ratio of hydrogen to nitrogen, but also by the overall *selectivity* of the complex catalytic system towards the possible nitrogenous end-products. Selectivity is a dynamic property resulting from a wide range of factors. Some of the aforementioned factors are pre-determined, essentially static ones (such as the chemistry of the TWC) and other highly variable parameters such as the temperature of the TWC and indeed the composition of the exhaust gas. So-called memory effects can also be of high importance, whereby operating conditions which have occurred in the recent history of the system can affect overall TWC performance and indeed selectivity [125], [126].

Hydrogen plays a wide range of roles in TWCs, and is well known to be highly active in the reduction of NO, although it is emphatically not the case that interactions between NO and H_2 inevitably lead to the formation of NH_3. However, indirect reaction pathways also exist, involving interaction of hydrogen with other molecules present in the exhaust gas stream. As a prime example, formation of NH_3 through hydrolysis of cyanates (which are known to be present in SI engine exhaust [127]) has also long been known to occur in TWCs, particularly where alumina is used as a support. The cases of HNCO and NH_3 have been reported to be intimately connected [50]; detailed studies and analysis of emissions of isocyanic acid and ammonia are available in [50]. The hydrolysis of cyanates to produce NH_3 can thus occur in two ways, one of which necessitates the involvement of a surface site and the other of which can occur in the gas phase [121] – the occurrence of two reactions (likely often in parallel) leads to a generally high reaction rate. Suppression of the formation of the isocyanate radical (NCO*) within the TWC has been suggested as a viable mechanism for controlling emissions of NH_3 [128].

While the carbonaceous, partially oxidised species CO might appear to have very little in common with NH_3, the very high availability of the species in SI exhaust gas and its involvement in secondary reactions occurring within TWCs means its plays crucial roles. A primary example of this is its very well-known involvement in WGS (10), that reaction being an important consumer of CO and producer of H_2. WGS and SR of hydrocarbons are highly relevant reactions determining the behaviour of TWCs, with implications for overall TWC functionality [129], i.e. extending well beyond the case of formation of NH_3 .

3.3. The magnitude of exhaust emissions of NH_3

At this point, it is worth repeating the clarification that emissions of NH_3 in this work are to be understood at tailpipe emissions, i.e. at the point of entry of the exhaust gas into the atmosphere, having passed through the aftertreatment system(s). When running on a range of petrol blends under both cold start and hot running driving conditions, mean NH_3 confrontations upstream of the TWC are often reported to be “negligible”, e.g. < 1 ppm [130]. Considering the accuracy of analysers commonly used in exhaust gas emissions testing and the overall potential for cross-readings from other compounds, possible contamination of the analyser’s sampling system, etc., it can be stated that NH_3 concentrations are at zero or near-zero levels. Such a view is strongly supported by the literature consensus, which states that engine-out NH_3 levels (i.e. those measured upstream of the TWC; or, for a system consisting of more than one TWC installed in series, upstream of the TWC closest to the ICE) can simply be negated in most contexts [131], [132]. The majority of the available literature published in the last 30 years on the subject of NH_3 emissions from vehicles does not report (or even mention) any significant levels of engine-out NH_3; however, studies such as [130], [132], [133], have confirmed experimentally that engine-out NH_3 concentrations are of very limited significance. A recent study on modern vehicles tested over two cold start driving cycles [134] showed measurable NH_3 concentrations upstream of the TWC in most cases, but found that post-TWC NH_3 concentrations were 45–72-times higher post-TWC, i.e. a discrepancy approaching two orders of magnitude, thus being essentially unanimous with the literature consensus on this point.

Focusing exclusively on tailpipe NH_3 emissions, the following brief compendium of emissions factors is presented. (Note that the compendium is selective and emphatically non-exhaustive.)

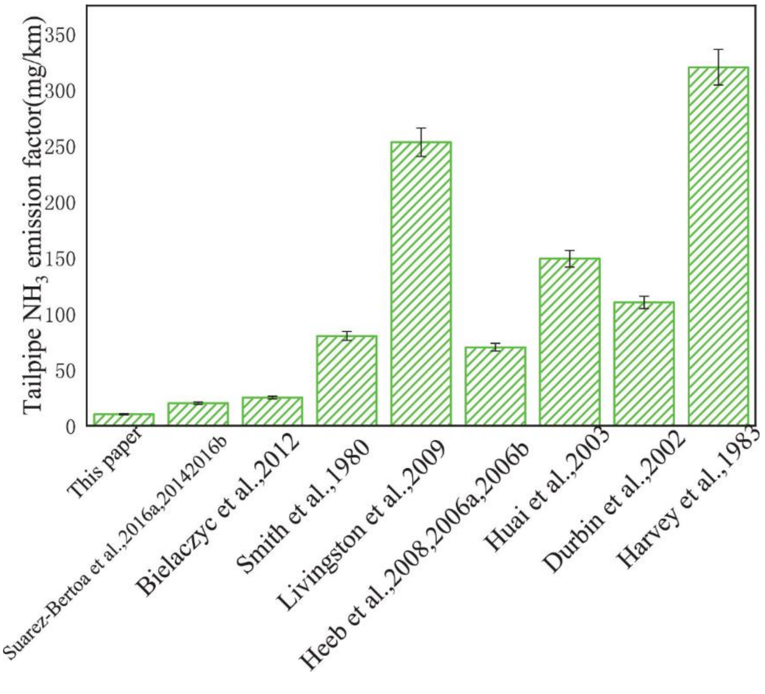


Figure 6. A compilation of overall NH_3 emissions factors from studies testing LD vehicles with SI engines. Image source: [134]; note that the text “This paper” refers to [134]

The available literature reports a wide range of emissions factors, which can vary by well over an order of magnitude. In terms of the distribution of emissions, the vast majority of laboratory studies employ too few vehicles to enable detailed intra-study examinations of the distribution of emissions levels. Inter-study comparisons are possible, but are subject to the usual cautionary constraints regarding test procedure, measurement equipment, etc. The literature contains several examples of compilations of emissions factors from various studies, two of which are shown below in Figure 6 and Figure 7.

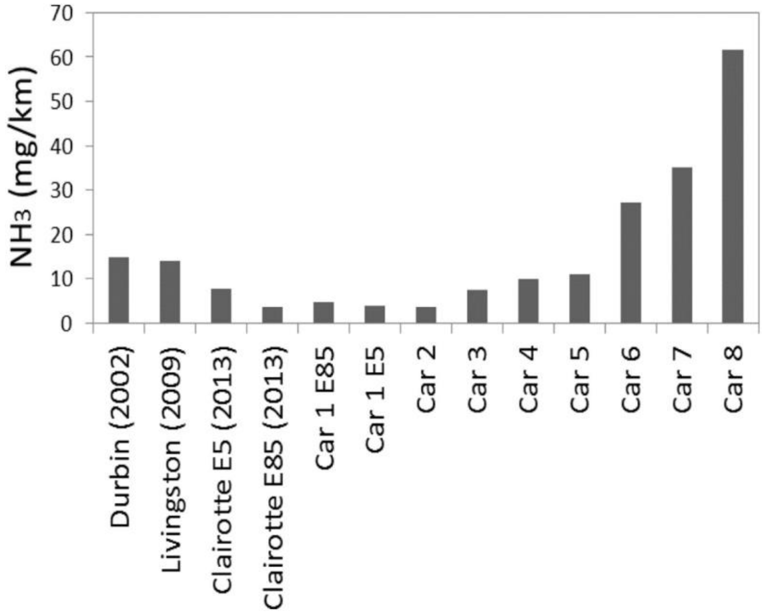


Figure 7. A compilation of overall NH_3 emissions factors from a single study testing LD vehicles with SI engines [85], alongside some comparisons from the literature. Results for Car 1–Car 8 are from the study itself [85]; image source: [85]

Note the fact that the range of emissions shown in Figure is approximately 5–60 mg/km, i.e. the range spans just over one order of magnitude.

A compendium of results from vehicles of broadly similar age, tested under a range of test conditions (driving cycles, ambient temperatures, start conditions) is available, as shown in Figure 8.

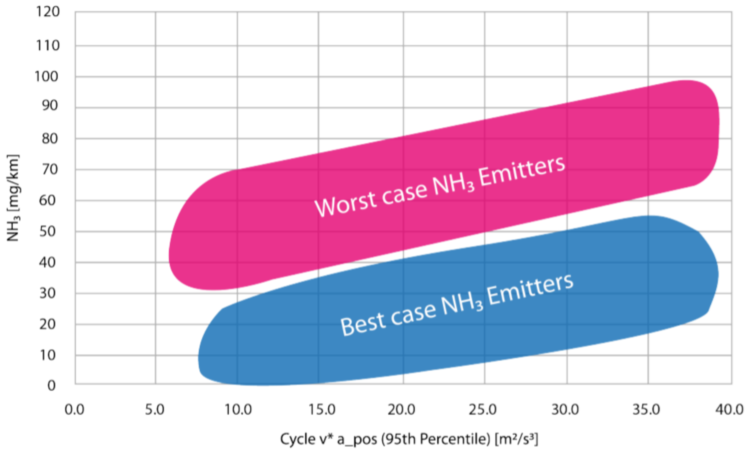


Figure 8. Compendium of NH_3 emissions results from various vehicles plotted as a function of the 95th percentile of the product of the velocity-acceleration product for the driving cycle used in each test. Image source: [135]

At the time of writing, the most recent study available in the literature, reporting NH_3 emissions from Euro 6d-TEMP and Euro 6d vehicles [136], reported NH_3 emissions within the range 1–16 mg/km, (with a single outlying value of 53 mg/km) over the WLTC cycle and 8–20 mg/km over a more demanding high-speed motorway cycle. Overall, lower NH_3 emissions were noted from hybrid vehicles.

Arguably the most authoritative available source of emissions factors for European vehicles can be found in the numerical tables for road transport [137] which contain the values used in the well-known COPERT emissions modelling program [138], [139]. This data source attempts to reduce the complexities of the wide range of vehicle types, emissions standards, and vehicle ages (and mileages), etc, to a single value for a given legislative emissions control level (i.e. Euro standard number) and given type of operating conditions (urban cold [start], urban hot [running], rural hot [running], highway hot [running]). Other studies conducted under the auspices of the COPERT project have provided input to the COPERT emissions factors (e.g. [140]). The COPERT emissions modelling tool [138] includes data parametrising the response of various vehicle types to increasing mileage. All coefficients given are positive (i.e. increases are expected to occur, as reported elsewhere – e.g. [141]), although the gradients are shallow amounting to very limited absolute increases which may be underestimates (cf. [141]). The COPERT model and its underlying data are widely referenced and even relied upon to provide input to other models and projections. The UK road transport emissions inventory gives breakdowns for various pollutants derived from sources including the COPERT database and COPERT input studies, as well as others. Of particularly note is the fact that complex and non-linear cold start NH_3 (and N_2O) emissions factors are reported for passenger cars by Euro class, as shown in Figure 9.

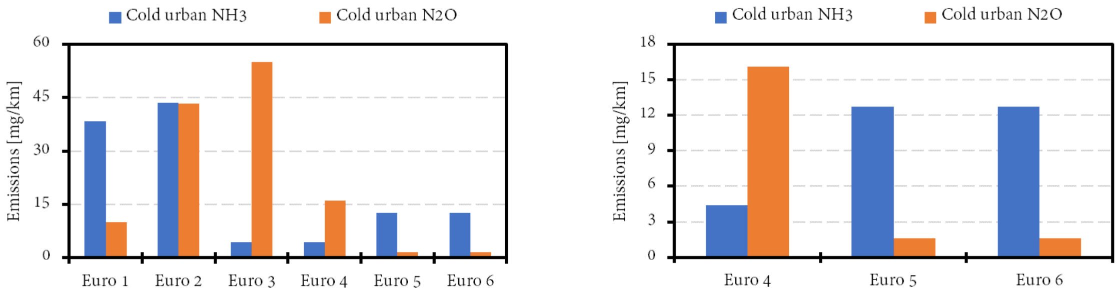
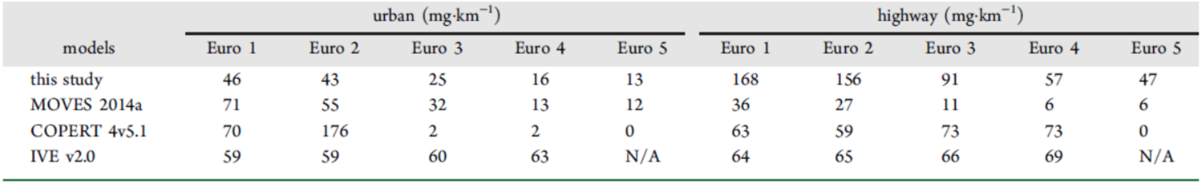


Figure 9. Figures: author's own; data source: [142]

a) NH_3 and N_2O emissions factors for cold urban driving for emissions control stages Euro 1–Euro 6

b) NH_3 and N_2O emissions factors for cold urban driving for emissions control stages Euro 4 –Euro 6

In contrast to the data presented above, the NH_3 EFs given in [139] are identical for Euro 4, 5 and 6 vehicles. Other studies have attempted to supplement or improve on MOVES, COPERT and IVE [143] in the range of NH_3 emissions. In [8] a model is developed which gives EFs for urban (thermal condition unspecified; assumed to be a mixture of cold start, warmup and hot running) and highway driving, as shown in the Figure 10 below.



models	urban (mg·km^{-1})					highway (mg·km^{-1})				
	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5
this study	46	43	25	16	13	168	156	91	57	47
MOVES 2014a	71	55	32	13	12	36	27	11	6	6
COPERT 4v5.1	70	176	2	2	0	63	59	73	73	0
IVE v2.0	59	59	60	63	N/A	64	65	66	69	N/A

Figure 10. A compilation of NH_3 EFs, divided by Euro class and by urban/highway operation; image source: [8]

The highway value shown above for Euro 5 vehicles is in relatively good agreement with [139], but the urban value of 13 mg/km is some 3.7 times higher than the mean of the urban cold (5 mg/km) and urban hot (2 mg/km) EFs given in [139], namely 3.5 mg/km. Despite models' attempts to provide universality, the influence of data considered for model development and calibration remains strong; especially where the numbers of vehicles considered is relatively low, outliers can significantly influence the final performance of the model. Indeed, multi-pollutant exhaust emissions models show variable performance, with NH_3 being subject to considerably greater uncertainties than other pollutants, mainly due to the fact that the majority of measurement campaigns (chassis dyno or PEMS) do not feature NH_3 measurement and thus data are limited [144]. General sampling and measurement issues peculiar to NH_3 also contribute to experimental error and estimates' general uncertainty.

The authors of [8] point out that the predictive power and overall quality of the model increase significantly when the combustion efficiency is known. This rather complex parameter can be approximated to the required high degree of accuracy based on exhaust emissions (termed "modified combustion efficiency"); which correlates very closely with post-TWC concentrations of CO (or, equivalently, tailpipe CO concentrations) [8]. This observation and modelling strategy is indeed entirely congruent with the strong theoretical and widely-reported empirical links between CO emissions and NH_3 emissions. As quantification of the concentration of CO in the exhaust gas is a fundamental emissions measurement practice, available even on the simplest and lowest cost emissions measurement systems, this provides a welcome indication that the accuracy of NH_3 models might be improved upon via inclusion of this parameter.

Remote sensing studies covering large numbers of vehicles appear a promising source of information in this regard. A comprehensive analysis of NH_3 emission factors conducted in urban areas in the USA revealed the log-normal distribution shown in Figure 11.

The distribution shown in Figure 11 supports the consensus that a large majority of vehicles are low NH_3 emitters, with many vehicles emitting no more than ~50 mgNH_3 per kg of fuel burned, with a small number of high emitters whose emissions can be over an order of magnitude higher than the overall characteristic EF for the fleet under consideration (e.g. mean, median or mode EF value). The number of vehicles which emit >1 g/kg-fuel should be very limited and vehicles emitting ~10 g/kg-fuel should be extremely rare. The aforementioned magnitude of emissions has been confirmed in other remote sensing studies (e.g. [146], [147]). A tendency has been reported for fuel-specific NH_3 emissions factors as quantified by remote sensing to be significantly lower for recent model year vehicles, at least in comparison to vehicles from the mid-to-late 1990s, as shown in Figure 12 – note the apparent non-monotonic trend, as well as the fact that the uncertainty and the spread present in the data appear to have reduced markedly over time.

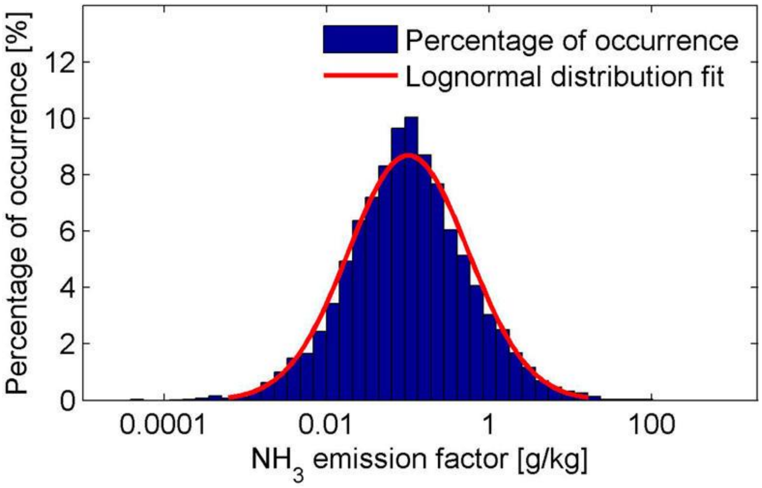


Figure 11. Histogram of fuel specific NH_3 emissions factors measured from a remote sensing study measuring vehicles under real-world operating conditions (note the $\log_{10}$ horizontal axis); image source: [145]

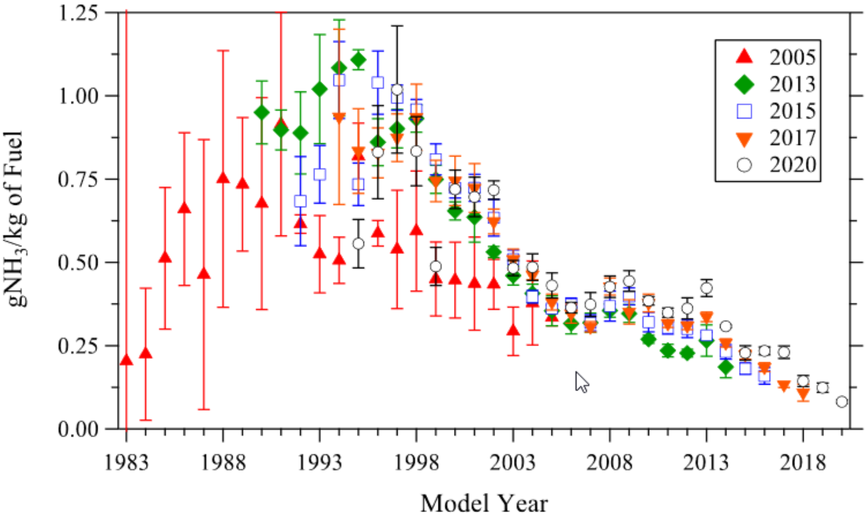


Figure 12. Fuel-specific NH_3 emissions factors as quantified by remote sensing, as a function of vehicle model year; image source: [147]

Further supporting this, a recent remote sensing measurement campaign in China [148] found that very few vehicles had an EF > 0.8 gNH_3/kg-fuel. The same study also reported that the 10% of highest emitters (i.e. percentiles 90–100) were responsible for some 38% of NH_3 emissions from all petrol-powered vehicles and around 30% for vehicles with SI engines running on alternative fuels. In terms of a broad comparison to distance-specific EFs, a fuel-specific EF of 1 g/kg-fuel is very approximately equivalent to a total 1 g of NH_3 emitted for a trip covering some ~15–20 km conducted under free-flowing (uncongested) urban conditions in a small passenger car with a conventional ICE. Such a scenario which would give distance-specific NH_3 emissions in the range of ~50 mg/km. For larger, significantly heavier vehicles (including vans and trucks) with engines of larger displacement, the distance travelled using 1 kg of fuel is lower and thus the distance-specific NH_3 emission factor would at least somewhat be higher, *ceteris paribus*. In conclusion, while the majority of the in-use fleet is characterised by low NH_3 emissions factors, even more so when focusing on recent model year vehicles, some modern vehicles have been found to emit ~1 gNH_3/kg-fuel. A further factor of relevance in considering fuel-specific emissions (of any type) is the fact that real-world fuel consumption remains at a higher level than is normally revealed under laboratory conditions, even when referring to results generated by laboratory test procedures derived from real-world vehicle usage data, such as the WLTP [149]. In terms of generalised comparisons with other sources and sectors, the aforementioned fuel-specific emissions factor of 1 gNH_3/kg-fuel is significant, since such a level is reported for NH_3 emissions from untreated flue gas resulting from the combustion of coal [150].

3.4. Consideration of exhaust emissions of NO_x in the context of analysing the existence and magnitude of NH_3 emissions

In the context of the present discussion, it is appropriate to comment on observations and tendencies for NO_x emissions from vehicles with SI powertrains, for several reasons. Firstly, NO_x is measured (and reported) in virtually all studies on emissions from light and HD vehicles, being subject to emissions limits applicable under laboratory conditions (and, increasingly, real-world conditions). Secondly, since NH_3 and NO_x are normally emitted under very different operating conditions, which are virtually mutually exclusive [117], examination of NO_x emissions behaviour can provide useful (albeit indirect) information on NH_3 emissions behaviour.

The majority of the literature reaches the conclusion that there is substantial evidence that the majority of Euro 5/6 vehicles with SI engines NO_x emissions take values significantly below the Euro 5/6 limit (often < 50% – i.e. ≤ 30 mg/km, and even ≤ 33% – i.e. < 20 mg/km), under laboratory conditions and even outside the laboratory under conditions broadly representative of real-world operation [12], [151], [152], [153], [154], [155], [156], [157], [158], [159], [160], [161], [162], [163], [164].

Regardless of emissions limits, NO_x emissions prior to TWC light-off (following cold start) are high, but distance-specific NO_x emissions tend to fall rapidly as distance accumulates beyond the time range required for the TWC's *light-off temperature*[4] for the species NO (NO T50) to be reached. Within the EU's legislative RDE testing framework, when commencing from a cold start, this causes NO_x emissions from stoichiometric SI engines to be highest for the initial, urban phase [165] of the test. Urban driving is inherently unstable and includes frequent periods of fuel cut-off. As is well-known (e.g. [166]), such events cause full oxidisation of the TWC components providing OSC and thus may be accompanied by the emissions of noteworthy quantities of NO_x.

When focusing on cold start operation, some 5 km of urban driving have been reported to be sufficient to reduce NO_x emissions from many passenger cars with Euro 6 SI engines to ~50 mg/km; having covered 20 km, all vehicles tested in that study had NO_x emissions which were significantly below that level [160]. Publicly available data from official RDE tests conducted on Euro 6 vehicles by manufacturers and authorised technical services [167] support this view [168], as well as other findings [165]. Other reviews and meta-studies have found that fleet hot running NO_x emissions from Euro 5/6 passenger cars rarely exceed a value of ~30 mg/km under standard urban, rural or motorway operating conditions [142]. An extensive and thorough remote sensing study confirmed the overall high general effectiveness of SI NO_x control via TWCs [169], an effect also noted for Euro 4 vehicles [158] as well as for many vehicles meeting recent US LD emissions standards [170], [171] (see also [146], [161], [172]). It has been asserted that some Euro 6 SI vehicles have lower NO_x emissions than equivalent Euro 5 vehicles (e.g. [12]), despite being subject to the same numerical emissions limits and – up to the Euro 6c sub-standard – precisely the same emissions type approval test procedure. Vehicles with various

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[4] This term is defined as the temperature at which a catalytic exhaust gas aftertreatment device (in this case a TWC) reaches a conversion efficiency of 50% for the first time. Where specified as NO T50, this refers to conversation efficiency for the species NO. Where unspecified, this refers to the value of T50 for the species CO (by convention).

types of hybrid powertrain have also been shown to generally have very low NO_x emissions, even under real world conditions and test regimes meeting (and even exceeding) the requirements for EU RDE testing (e.g. [173], [174], [175]), as well as at sub-zero ambient temperatures (e.g. [175], [176]). Similar trends have been reported from some HD vehicles with SI powertrains fuelled with CNG/LNG (e.g. [177]); data have shown distance-specific NO_x emissions generally on the order of ~200 mg/km and sometimes as low as ~70 mg/km, for vehicles powered by SI ICEs of displacement ~9 dm^3 propelling a total mass around 31 tonnes [178]. Real-world PEMS testing of Euro VI trucks and buses of laden mass 8-16 tonnes with CNG powertrains with a TWC (but no SCR) over mixed routes commencing from a cold start has revealed that distance-specific NO_x emissions are for the most part within the range 100-200 mg/km [179]. Similar NO_x emissions from US HD trucks with SI engines have been reported elsewhere (e.g. [180]).

While certain exceedances of emissions limits have been noted for such vehicles under real-world conditions [181], a broad measuring campaign revealed NO_x emissions to be reasonably close to legislative limits, with very little dependence on the temperature of the aftertreatment system [181][5]. Nevertheless, a surprising degree of scatter has been reported in terms of the proportion of total NO_x emissions emitted during the first 1-2% of the driving distance of an RDE test [162], that distance being roughly equivalent to the cold start period (as defined in RDE requirements).

In strong contrast to the case of CI engines, NO_x emissions from vehicles with SI powertrains fitted with TWCs are, *ceteris paribus*, often somewhat better controlled during periods of high power demand (which may be quantified by VSP values or by the instantaneous normalised power developed by the engine) [182], [183], [184]. This oft-repeated observation can be mainly attributed to the common use of $\lambda < 1$ during such events. As is very well known (e.g. [3], [71]), where the temperature is above NO T50, the NO_x reduction process within the TWC proceeds with high efficiency under reducing conditions, which are precisely the conditions identified as being associated with TWC-facilitated formation of NH_3.

In consideration of the above, a highly pertinent question arises as what extent these generally low NO_x emissions have been achieved at the cost of elevated NH_3 emissions, NH_3 emissions not having been measured in the vast majority of studies examining this topic. A question also arises as to whether the vehicles and testing scenarios which revealed higher NO_x emissions were associated with lower NH3 emissions, and vice-versa.

3.5. The impact of powertrain design and characteristics on NH_3 emissions

During the literature review, very few studies were found which dealt explicitly with the link between powertrain design and characteristics and NH_3 emissions. Before the turn of the millennium, some comparisons of NH_3 emissions between vehicles with SI and CI engines, or between SI vehicles with and without aftertreatment are to be found in the literature, but such comparisons are now facile, since those aspects are well understood. Certain powertrain design parameters are considered in detail in the following sections, as well as in the experimental work presented in this thesis.

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[5] It is to be assumed that this statement by the authors does not extend to cold start and the initial period of engine operation during which aftertreatment system warmup occurs.

3.6. The impact of ambient temperature on NH_3 emissions

While ambient temperature itself has a reasonably limited impact on the spark ignition combustion process itself – at least following the first few cycles of engine operation, it is well known to cause a range of effects which themselves are of great importance in determining engine operation, fuel consumption and emissions [185], [186], especially during the initial period of engine operation (before powertrain – and especially aftertreatment system – warmup has been achieved). A further consideration is the warmup of the TWC, which for cold start commences from ambient temperature, by definition. In cases of ambient temperatures below room temperature and near- or sub-zero temperatures, the initial temperature of the TWC is lower, yet this difference is small compared to the ΔT required to reach typical T50 temperatures. As NO T50 is widely reported to take values of approximately 200°C, the ΔT is approximately 180°C where ambient temperature is 20°C, but the ΔT is approximately 205°C for an ambient temperature of –5°C. Thus, a large difference from the anthropocentric point of view (for example, summer vs winter) leads to a difference in ΔT of only some 12%. Various counteracting effects mean that formation of NO_x within an SI engine shows a noticeable but relatively modest response to large changes in ambient temperature, as shown by a sample measurement in Figure 13.

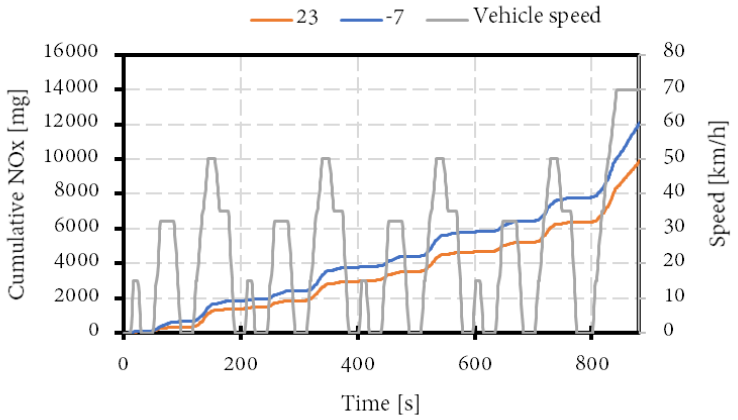

Figure 13. Pre-TWC cumulative NO_x emissions measured from a passenger car with an SI engine running over the majority of the NEDC at two different ambient temperatures (+23°C, –7°C)

The data shown in Figure 13 are engine-out NO_x emissions taken from cold start testing at +23°C and at –7°C (mean of two tests performed at each temperature, with both tests being in very good agreement with each other). Differences in emissions associated with engine startup and the first ~1 km of vehicle operation amounted to around 20%. After 4 km of low load urban driving, the total quantity of NO_x emitted was just under 25% higher at the lower test temperature. Applying higher load (e.g. acceleration to 70 km/h, followed by a few seconds of cruising at that speed in top gear, as shown on the right side of the speed trace in Figure 13) again caused NOx emissions to be some 20% greater at the lower test temperature. For driving at higher speed under thermally stabilised conditions, differences remain but are diminished in magnitude.

As ambient temperatures are always << TWC T50, ambient temperature is of very low relevance for the activity of the TWC at cold engine start-up and the time taken to achieve T50 depends much more strongly on the engine calibration (especially λ) and the enthalpy of the exhaust gas than on the ambient temperature itself.[6] Furthermore, it is worth recalling that for cold start at all ambient temperatures – but especially so at low and sub-zero ambient temperatures – as the NO T50 of a close-coupled TWC is

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[6] At least for technologies currently applied in commercial automotive applications.

approached, the composition of the gas entering the TWC typically remains subject to the effects of additional fuel enrichment.

As such, notwithstanding the increased availability of non-NO_x precursors for potential NH_3 formation reactions (H_2, but also THC and CO, especially considering SR and WGS), the roughly comparable level of NO_x formed within the engine may be the key factor – and as such, the massive THC and CO emissions excesses occurring at cold start at low ambient temperature largely fail to translate into similarly excessive emissions of ammonia. Increased NH_3 emissions at low (sub-zero) ambient temperatures have been reported in some studies [151], [151], [50], [187], [136]. Suarez-Bertoa and Astorga (2017) [188] tested several passenger cars with SI engines at –7°C and at +23°C, reporting increases in NH_3 emissions by a factor of 1.5 (range: 1.1-1.6) in response to the aforementioned change in ambient temperature. A similar study [189] reported somewhat higher emissions at –7°C compared to +23°C, but with a modest difference in the median NH_3 emissions values from those two test temperatures; significantly greater dispersion was noted at the lower test temperature, suggesting increased sensitivity of formation and/or quantification at such temperatures. For a cold start driving cycle, the effect where the water vapour generated by combustion (and in the TWC) condenses on cold metal surfaces in the exhaust line (and thereby acts as a trap for various gaseous emissions, including ammonia is considerably stronger at low ambient temperatures. (See [190] for a discussion of such effects and their impacts on emissions measurements.) Ammonia is highly soluble in liquid water, forming what is termed ammonium hydroxide, but this aqueous solution cannot exist as gas; solubility decreases as temperature increases and the final boiling points of ammonium hydroxide solutions of various strengths are significantly below 100°C (in some cases roughly 30°C), meaning that NH_3 outgassing is assured as the temperatures of the metal surfaces of the exhaust line increase. Such an effect does not reduce significantly reduce emissions in the long term, but it may noticeably delay release (and subsequent detection) of NH_3 molecules. The solid deposits (chiefly ammonium nitrate) which can form in NH_3-SCR systems used in CI powertrains should not be expected to survive in the exhaust line of an SI powertrain, owing to the temperature consistently being >200°C during normal driving and also due to the very low proportion of NO_x in the exhaust gas which occurs as NO_2.

Over driving cycles of normal length conducted at room temperature, the aforementioned outgassing phenomenon is likely to make itself at least somewhat evident. In extreme cases (particularly for very short driving cycles conducted at low or very low ambient temperatures) the test vehicle may still have a significant quantity of ammonia-bearing water in its exhaust line at the end of the emissions test, thus making NH_3 emissions artificially low [115] and creating a strong scale-dependent sampling artefact, since extending the sampling period (i.e. extending the duration of the test by, say, 20%) might lead to the quantification of a much larger quantity of NH_3. This situation might even distort the relationship between engine operating metrics during the test cycle the NH_3 emissions results – if a test cycle of the type mentioned above is extended by adding low load operation (or even idling) at the end, the cycle's mean demanded power, mean vehicle speed, mean engine rotational speed, etc will fall, but the total ammonia emissions could in fact increase, due to the release and quantification of so-called "latent ammonia".

On the subject of scale-dependent effects, a trivial yet relevant fact should be noted – namely, that the number of kilometres covered by a cold start driving cycle bears a great deal of influence on the emissions impact of the cold start event. For example, the NEDC covers 11 km and does not exceed a speed of 50 km/h until some 68% of the total cycle time has elapsed; self-evidently, this is not directly comparable to the WLTC, which covers over 23 km and where a speed of 50 km is first exceeded after only 12% of the total cycle time has elapsed. Many on-road tests performed on light-duty vehicles cover a much higher number of kilometres (~50–100), lasting up to around 1.5 hours and thus giving the cold start event a very low weighing in the overall test result. Such considerations may limit the ability to reliably transfer and extrapolate results and are likely to make NH_3 emissions' responses to changes in ambient temperature cycle-specific.

3.7. The impact of fuel type on NH_3 emissions

While the terms "petrol engine" and "gasoline engine' are often used interchangeably with "spark ignition engine", such a definition is unsatisfactory, since such engines can run on a very wide range of hydrocarbons and organic molecules, supplied to the engine in liquid or indeed gaseous form. The majority of SI engines used in road transport run on petrol, yet this generic term does not have a fixed composition and globally there is considerable variation in composition. A minority of SI engines used in road transport run on the alternative fuels LPG, CNG, E85 and even pure hydrous ethanol, either in part or in full. Thus, taking into consideration the full range of fuel types in common use, the range is found to comprise both the liquid and gaseous phases, as well as a very wide range of compounds, ranging from methane to alcohols and aromatic molecules of molecular weight > 100 Da. As regards petrol, a significant differentiator of the petrol available between different parts of the world and between current fuels and those sold in previous decades is the presence of oxygenated organic molecules, chiefly ethanol. A further consideration is the permitted maximum level of the heteroatom sulphur in the fuel, which remains high in a few markets where exhaust aftertreatment commonly fitted to new (or imported) vehicles.

In most automotive markets, fuel parameters are closely controlled and the range of permitted values for multiple key parameters is limited by law. This also applies to alternative fuels – LPG and CNG, as well as to market available petrol blends containing higher levels of ethanol (e.g. E85). However, there is scope within the framework of the law for substantial variation from fuel to fuel. As one of the major trends of recent years regarding fuel for SI engine shas been the addition of oxygenates (now chiefly ethanol), fuel ethanol content is a parameter worth examining in the context of its impact on NH_3 emissions. The latest type approval procedures for petrol-fuelled vehicles calls for E10 fuel to be used; nevertheless, the vast majority of petrol sold in the EU remains E5, with some very limited quantities of E0 also sold. Investigations into the use of fuels containing varying levels of ethanol have shown measurable – but generally modest – differences in NH_3 emissions as a result of changes in fuel ethanol content (e.g. [130], [132], [191], [192], [193], [194]). The overall finding is for the presence of ethanol in fuel to reduce NH_3 emissions somewhat, but effects are often non-monotonic, inconsisitent and of limited magnitude. Even very large changes in fuel ethanol level (such as when moving from E5 to E85) are reported to cause noticeable yet modest changes in NH_3 emissions (e.g. [50], [130], [195]), at least in engines designed to make use of high ethanol blends. Similar trends have been reported for butanol-petrol blends [196], whereby measurable differences in NH_3 emissions are reported, but such changes are modest, and of lower magnitude than differences observed between vehicles or those resulting from variable operating conditions. However, a further complicating factor is that the sample transport (and indeed sample loss) behaviour may vary for different fuel types tested in the same vehicle, particularly for cold start testing procedures conducted at lower ambient temperatures, where condensation effects are self-evidently of greater relevance. The NH_3 emissions behaviour reported in [196] may be reflective of such effects; in such cases it would be unwise to attribute observed differences to the inherent NH_3 formation propensity of a given fuel. For example, the correlation between fuel butanol content and mean NH_3 concentration during the initial ~600 seconds if idling evident at an ambient temperature of 0°C is both of questionable significance and in fact inverted at an ambient temperature of 20°C, as shown in Figure 14.

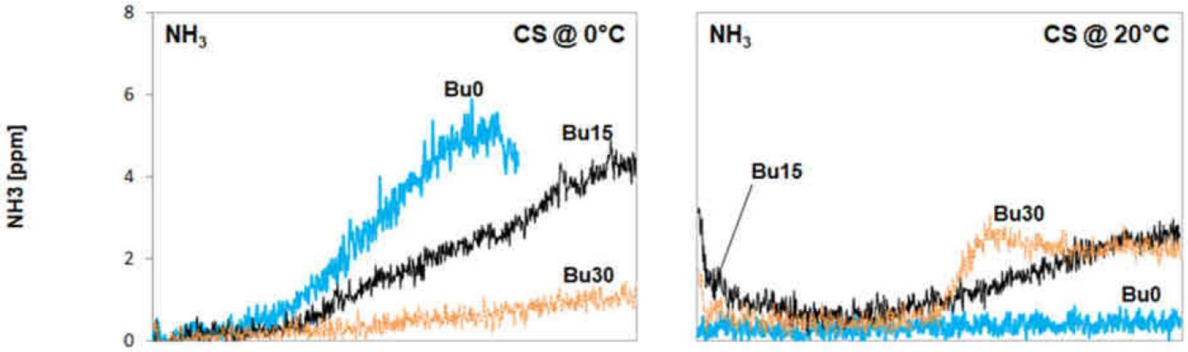

Figure 14. NH_3 concentration traces for 3 fuels tested in a vehicle over a 900-second idling cycle at two ambient temperatures. CS – cold start. Bu*x* corresponds to the butanol level of the fuel (*x*%); the horizontal axis of each image corresponds to 0–900 seconds; image source: [196]

A detailed study testing a range of alcohol-containing fuels, including testing at low ambient temperatures, revealed certain differences between NH_3 emissions as a function of the fuel blend under test. However, the choice of test procedure (NEDC, WLTC) was found to exert an impact of comparable magnitude to that resulting from the use of different fuel blends, as shown in Figure 15.

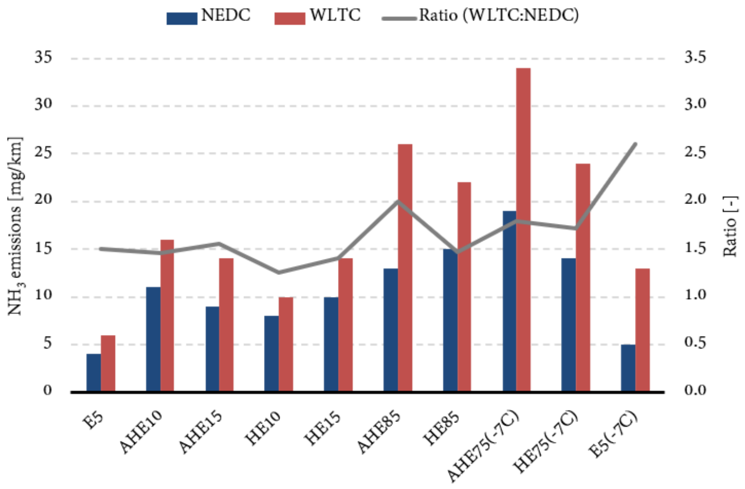

Figure 15. NH_3 emissions from a single test vehicle, tested on a range of fuel blends, using two test procedures (NEDC, WLTC), including tests at low ambient temperature. Data source: [191]; figure: author's own

A large number of detailed studies of the impact of alcohol content on exhaust emissions are available, but the vast majority of studies do not include NH_3 measurements, due to the legal status of the compound in the automotive context. Reinforcing the points mentioned above, detailed investigations of NH_3 emissions from a single tetra-fuel vehicle running on multiple fuel types [193] found that the driving cycle used for testing had a much greater impact on NH_3 emissions than the fuel type; similar conclusions were reached in another study [194]. However, the addition of ethanol to petrol is a non-trivial subject, since multiple properties of the resulting blend are altered, including, inter alia, the volumetric proportion of aromatic compounds, density, octane number, etc. Studies reporting the NH_3 emissions resulting from usage of different fuels (or fuel blends) in the same vehicle must be interpreted with care, since the properties of the base fuel to which ethanol (or any other blend component) was added may not have remained constant, or indeed may have been deliberately altered, in order to compensate for the properties of the ethanol. Such blend properties can have impacts on emissions which may be attributed erroneously – or at least somewhat improperly – to the fuel ethanol level itself [197].

Fuel chemistry has indeed been confirmed to be relevant in terms of the availability of bound hydrogen – the presence of unsaturated hydrocarbons has been shown to cause a large increase in TWC-facilitated NH_3 formation, which was attributed to the increased availability of hydrogen from those hydrocarbon molecules [198]. This would imply that standard petrol, of which some ~30% of the volume is made up of unsaturated aromatics, might cause substantially different behaviour than LPG (propane-butane) and CNG (methane), which, despite containing some higher hydrocarbons, contain very low levels of saturated hydrocarbons. However, the literature contains few such studies and the picture presented can be described as mixed. A further complicating factor is that many CNG- and LPG-fuelled vehicles run on petrol for some time following cold start.

The impact of natural gas composition on resulting exhaust emissions of various gaseous compounds (including NH_3) from a HD vehicle under real-world (on-road operating conditions) has been investigated [199]. Ammonia emissions results showed varying responses to the six gaseous fuels used, with the difference between the lowest and highest result being some 36%; increasing N_2 and increasing C:H ratio were associated with higher NH_3 emissions.

A further study [200] also concluded that natural gas composition exerted a significant impact on NH_3 emissions. The main stated finding was that the heating value of the gas was proportional to the NH_3 production rate, thus replicating and reiterating one of the findings of [199]. Another study testing a single fuel found NH3 emissions from a HD CNG vehicle tested under real world conditions over several routes to take values of around 1 g/mile (~0.6 g/km) [201]. A detailed review of the impact of hydrogen-enriched NG on exhaust emissions is available [202], but NH_3 emissions were not considered. (However, significant changes to engine-out NO_x levels were reported.)

Bi-fuel vehicles sometimes show significant changes in NH_3 emissions when comparing use of one supported fuel type to the other under given test conditions (e.g. [132], [203], [193]) but results can be contradictory, making generalisation difficult. A further layer of complexity results from the fact that bi-fuel CNG vehicles normally feature CNG-specific TWCs, which can differ in multiple respects from the TWCs fitted to mono-fuel petrol counterparts, specifically often featuring Pd loading which is high (or very high) in comparison [204], [205].

Sulphur has a long history of causing problems with exhaust gas aftertreatment [206]. The fundamental problem stems from the fact that sulphur dioxide resulting from combustion of S atoms has a tendency to adsorb to the active sites in a TWC. This reduces the number of available active sites for the desired reactions through a range of mechanisms, including steric effects, as well as complex electrochemical interactions with surface species (PGM) and also the support. The precise mechanisms of poisoning are highly complex, yet the general highly detrimental effect of sulphur on catalytic aftertreatment (including TWCs) has long been known (e.g. [207], [208]). This has caused markets with stringent emissions requirements to limit the sulphur content of fuel to very low levels; this requirement was also extended to engine lubricants (albeit more slowly and with much less rigorous limits than in the case of fuel). Nevertheless, over extended timescales equivalent to tens of thousands of kilometres and years of normal powertrain usage, sulphur can begin to exert an impact on TWC functionality, even where the S level in the fuel (and indeed lubricant) are very low. Furthermore, alternative fuels such as LPG and CNG can show noticeably higher sulphur levels than many market-available liquid fuels.

A study examining the short-term impact of LPG sulphur level [209] found NH_3 to increase slightly with fuel S level under all driving conditions tested, although the magnitude of the short-term impact was relatively weak when comparing 4 ppmS and 40 ppmS fuel. (Interestingly, that study also reported a similar effect for NO_x emissions.) Another recent study found that TWC ageing on fuel of higher sulphur content reduced the NH_3 yield [210]. Potential explanations for contradictory results in this area include the result of variable and highly complex PGM-support compositions, which have in fact been long recognised (e.g. [106]). A 2018 study [211] found that accelerated ageing on sulphur-bearing fuel increased N_2O yield and decreased NH_3 yield, at least in certain cases.

3.8. The impact of TWC parameters on NH_3 emissions

3.8.1. Inherent TWC composition

When considering TWC chemistry in the context of a given TWC's propensity to create ammonia, two points are worth keeping in mind: firstly, that the PGMs used in such a device are costly and that the relative prices of the various metals can fluctuate significantly; secondly, that since the vast majority of vehicles with SI ICEs sold globally are not subject to an NH_3 emissions limit of any kind, the impact of changes to TWC chemistry on NH_3 emissions has – historically at least – not been of particular concern to TWC manufacturers.

At the time of writing, the majority of TWCs feature palladium (Pd) and rhodium (Rh). Platinum (Pt) was in widespread use in TWCs until relatively recently, but its use fell sharply, to the point where it was used in a minority of cases, a change which occurred for economic as well as technical reasons [212], [213]. This situation would appear to be changing; cautious optimism has been expressed regarding a wide-scale return of Pt to TWC applications [214] and indeed this process is arguably now in progress [215].

The generalised statement or overall inference that Rh is the PGM solely responsible for reduction of NO_x can be found in the literature – yet this is a gross oversimplification, since TWCs without any Rh also show appreciable NO conversion rates [123]. The presence of even a small quantity of Rh is well known to be highly beneficial for overall TWC performance, and particularly for NO_x conversion [216], especially where quantified during test procedures dominated by a cold start event [212]. Rh strongly promotes the conversion of NO_x [212], [216], being highly active in the reduction of NO by CO [217], yet this is not unique, since Pd and Pt (as well as certain other metals, such as iridium (Ir)) also show considerable catalytic activity in such reactions. Some experimental evidence obtained in the 1970s [218], [95] showed increased NH_3 formation for Pt-Rh and Pd-Rh compared to Rh alone, a consensus which was reiterated in the 1990s [219] and has largely withstood the test of time, since no comprehensively contradictory experimental results are evident in the literature. A recent study [220] comparing Rh, Pd and Pd-Rh TWCs found that Rh generated the lowest amount of NH_3 (but the highest amount of N_2O)[7], while Pd generated the highest amount of NH_3. It has been reported that Pt is capable of promoting formation of NH_3 at very low temperatures (< 200°C) [121], behaviour which is normally not observed with Pd nor with Rh. Such behaviour has obvious implications for NH_3 emissions profiles over cold start driving cycles, where Pt is present in the TWC.

In terms of selectivity, Rh has been reported to be emphatically much more selective towards N_2 than Pt [221], although the authors of that study did not include Pd in their comparison. The complicating factor of selectivity towards N_2O means the system is emphatically non-binary and suggests that important trade-off effects could be present [220]. Extrapolations from direct comparisons of

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[7] The existence of NH_3-N_2O trade-off emissions profiles are noteworthy; however, the TWC temperature range for substantial N_2O formation is well known to be both low and narrow.

commercial TWCs or research samples and prototype systems containing different PGMs (e.g. [222]) can be problematic, since many other details may differ between samples, such as the PGM loading, physicochemical characteristics of the support, OSC behaviour, etc. Atomic configuration also appears to play a key role; indeed, it has been reported that single Rh *atoms* are 100% selective to NH_3, while Rh *nanoparticles* have high selectivity to N_2 [217], [223]. Self-evidently, such nanoscale specifics of the PGM configuration cannot be adequately described in the terms of the nomenclature commonly used in automotive applications (the relative PGM ratio and total PGM loading). PGM atom distribution will not be further commented on here, but the topic is of high relevance and could also be involved in ageing-induced changes in selectivity of a given TWC.

A study [224] comparing Pt-Rh and Pd-Rh samples of identical X-Rh ratio (5:1) and identical total PGM loading found that while differences in NH_3 formation were detectable, trends were in fact similar. When tested at three different temperatures, the boundary λ value for the onset of NH_3 production was essentially identical for both samples. There was, however, a tendency for NH_3 production over Pd-Rh to be lower than that of Pt-Rh at λ values relatively to close to 1; for richer mixtures with higher redox ratios, the situation was reversed and Pd-Rh caused higher production than Pt-Rh.

Figure 16 shows how the same PGM (in this case, Pd) on different supports can significantly alter selectivity towards NH_3 (see also [106]). What is more, the differences are somewhat temperature dependent and also vary strongly with feed gas composition. Indeed, as also shown in [225], the selectivity of a given PGM-metal oxide combination can be strongly altered by the level of CO (*ceteris paribus*).

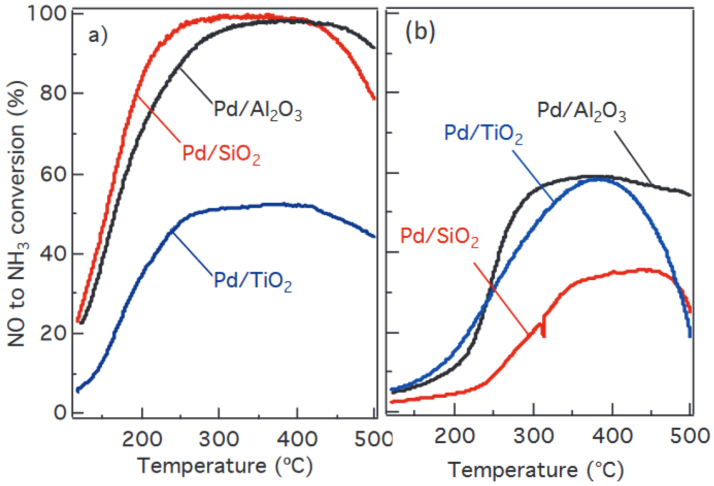

Figure 16. The impact of support material (Al_2O_3, SiO_2, TiO_2) on the conversion of NO to NH_3, for two different simulated exhaust gas mixtures. Note the fact that the maxima of all curves occur at temperatures < 500°C. Image source: [225]

The propensity of the PGM-support combination to hydrolyse HNCO to NH_3 [226] is likely of relevance in explaining such effects. Further evidence of such effects was provided by a detailed investigation of the reduction of NO by H_2 over Pt, Pd, Rh and Ir catalysts supported by four different metal oxides [123]. As Figure 17 summarises, the PGM, the support and the temperature all exert varying influences on the selectivity. A notable feature is the high (~50% selectivity of Pd at 400°C over Al_2O_3, CeO_2 and ZrO_2, which was even higher over SiO_2. Such behaviour underlines the impact of support-PGM interactions and synergies for Pt and Pd, but the other panels in the figure also show that these effects are far weaker for Rh and Ir. In other words, when comparing Pd and Rh based on that experimental evidence, the NH_3 formation propensity of the former is a much stronger function of the PGM-support combination; Rh's inherent properties – almost irrespective of the support – control its NH_3 formation [123]; this appears to also apply to N_2O [220]. For all PGMs over all supports, a general tendency for selectivity towards NH_3 to decrease at increasing temperatures was observed, although in all cases the trends were non-monotonic. The fact that a single feed gas composition consisting of NO and H_2 in a 1:1 molar ratio (remainder inert) is significant for two reasons: firstly, hydrocarbons and water were absent, and – crucially – no CO was present; secondly, the molar ratio of 1:1 is self-evidently below the critical stoichiometric ratio of 5:2 mentioned earlier, yet nevertheless substantial NH_3 selectivity (up to ~75%) was observed.

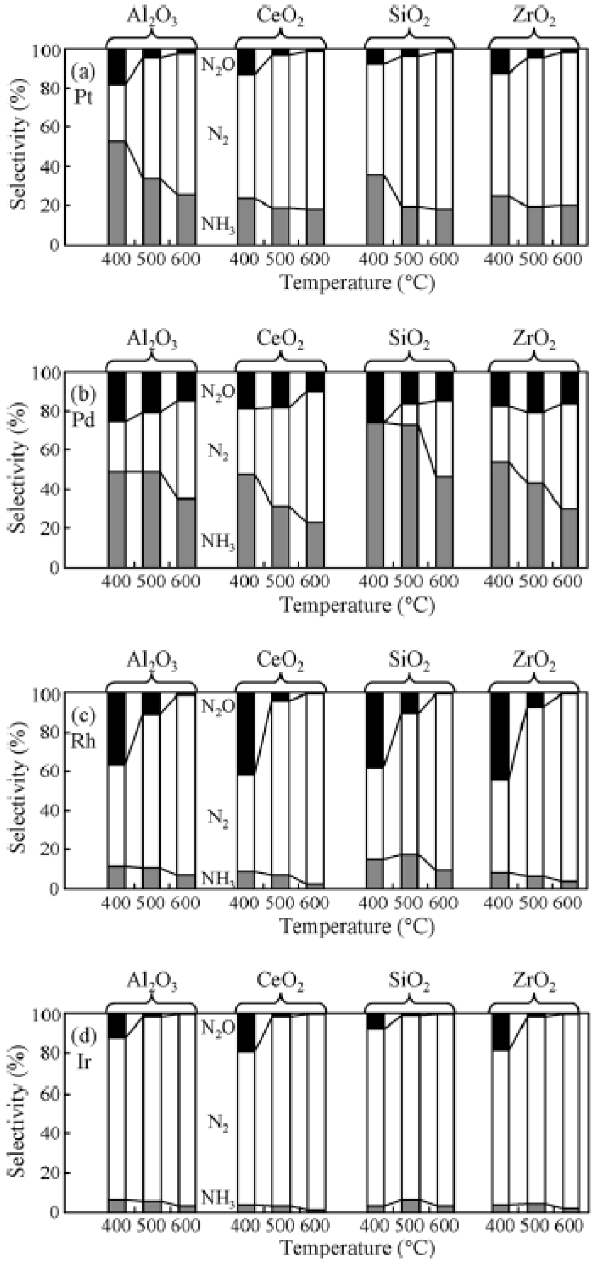

Figure 17. Trinary RNC selectivity for a single simulated exhaust gas mixture, for the cases of four different PGM promotors: a) Pt, b) Pd, c) Rh, d) Ir, four different support materials and three different temperatures; image source: [123]

In summation, considering the available literature published since the early 1970s to the time of writing, the following overall ranking regarding the propensity for NH_3 formation may be posited: Pd > Pt > Rh. However, for Pd and Pt tendencies are strongly influenced by PGM-support interactions (see [227]), while Rh's behaviour appears to be more of a function of that metal's specific properties (and abundance).

Such observations suggest that considerable optimisation of commercialised TWC formulations (the PGM-support combination) to modify nitrogen partitioning, maximise selectivity to N2 and thereby reduce NH_3 (and N_2O) emissions is possible. Such an approach might be described as "RNC-optimised".

3.8.2. TWC ageing, degradation and the presence of impurities

Since a TWC is exposed to a high temperature gas stream containing CO and a range of hydrocarbons – as well as very high levels of H_2O – the entire time the engine is being fuelled, deterioration in system performance is well known to occur and can be considered inevitable. Where these processes occur as a result of normal real-world (i.e. naturally and often relatively gradually), the collective set of phenomena is generally known as *TWC deactivation*. Several mechanisms have been identified, which may be divided into three basic categories: thermal, chemical and mechanical (see [207], [228] and references therein for detailed discussions). Essentially every mechanism is experienced by every in-use TWC, with effects differing only in terms of severity and relative importance from case to case. As fuels used in markets with advanced emissions control requirements (such as the EU) are generally of high quality, in recent years assessments have often focused primarily on thermal deactivation phenomena (e.g. [229], [230]), although the impact of heteroatom impurities (most notoriously sulphur, but other elements including phosphorous are still important and should not be negated [231]).

As regards the impact of such effects on NH_3 emissions, there are two main scenarios to be noted. Firstly, broad and general deactivation of the TWC may occur, as a result of which the TWC partially loses its ability to catalyse reactions leading to the elimination of regulated pollutants and thus the system loses its $DeNO_x$ capability. In such a scenario, even though the conversion of NO to NH_3 is an undesired reaction, basic principles of catalysis would suggest that it is likely to be affected in manner comparable to that of desired reactions of similar type (i.e. reduction of NO to N_2). In such cases (*ceteris paribus*), a decrease in the concentration of NH_3 in the exhaust gas should be seen, together with an increase in the concentration of NO_x, since a greater proportion of NO_x is simply passing through the TWC without entering into any reaction – desired or otherwise. Such behaviour has recently been reported in the context of emissions from a motorcycle undergoing mileage accumulation [232]. This can be explained in very simple terms, since by definition, as the $DeNO_x$ ability of the TWC falls, the proportion of the NO_x entering the TWC which leaves in the same form necessarily increases. Where such a mechanism is at work, decreases in the elimination effectiveness of species other than NO_x might also be noted, as indeed has been reported in some studies (e.g. [233]). As engine-out NO_x emissions from LD SI engines can be as much as two orders of magnitude higher than NO_x emissions limits, even small reductions in the $DeNO_x$ effectiveness result in elevated emissions, which can easily be detected under laboratory conditions.

Secondly, and concurrently, physicochemical changes could occur which impact overall system NH_3 selectivity. A situation could occur where the $DeNO_x$ effectiveness is unchanged (or somewhat decreased but still acceptably high), yet the TWC has suffered undergone physicochemical changes meaning that the ability of the TWC to catalyse NH_3-forming reactions has been altered. Structural changes are known to occur and to be able to affect general catalyst selectivity in additional to overall activity [234]. An example of such a situation would be where the overall selectivity towards N_2 reduces and as a result the concentration of NH_3 (and/or N_2O) increases (for a given NO_x input concentration). In the absence of available NH_3 measurements, such a situation would be difficult to detect, since the post-TWC NO_x concentration might be unchanged (or at least similar) in comparison to the level before the ageing took place. In such a scenario, the overall $DeNO_x$ effectiveness (and legislative compliance) remain entirely unaffected.

Experimental data on NH_3 selectivity as a function of ageing presented in [235] were severely overfitted, giving rise to a 3rd order polynomial equation of dubious predictive power. A power-law fit yielded a relationship which is likely of greater physical significance and predictive power, as shown in Figure 18.

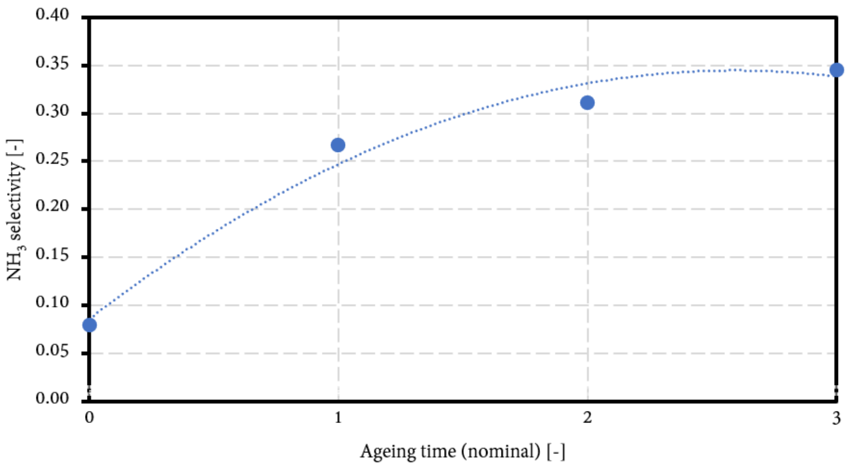

Figure 18. Impact of progressive TWC ageing on NH_3 selectivity; data source: [235]

This trend shows that initial ageing causes the greatest deterioration, but that the rate of later decreases. The trendline implies that further ageing – perhaps in combination with or conducting more frequent testing during the ageing process – might reveal an asymptotic relationship, perhaps tending towards a value in the region of 0.4. Such a level would be some 4 times higher than the selectivity reported before any ageing was carried out (i.e. at ageing time = 0). In this context, it is worth noting that TWC ageing has been linked to increased N_2O emissions [236].

Monitoring of real-world emissions of vehicles meeting a certain emissions standards (e.g. Euro level), parametrised by vehicle age, show relatively modest increases in NH_3 emissions as vehicle age increases, as shown in Figure 19.

As regards real-world NH_3 emissions measured from the US fleet, Bishop et al. state that NH_3 emissions first increase and then decrease with increasing vehicle mileage (see [238] and references therein, especially [239]). Similar trends had been reported previously for US passenger cars, as discussed in [119]. Other studies (e.g. [141], [240]) have reported that NH_3 emissions increase as vehicle mileage increases, yet despite reports of monotonic deterioration [141], the picture presented in the literature is mixed and at the fleet level the effect may be weak (or even non-existent in some cases).

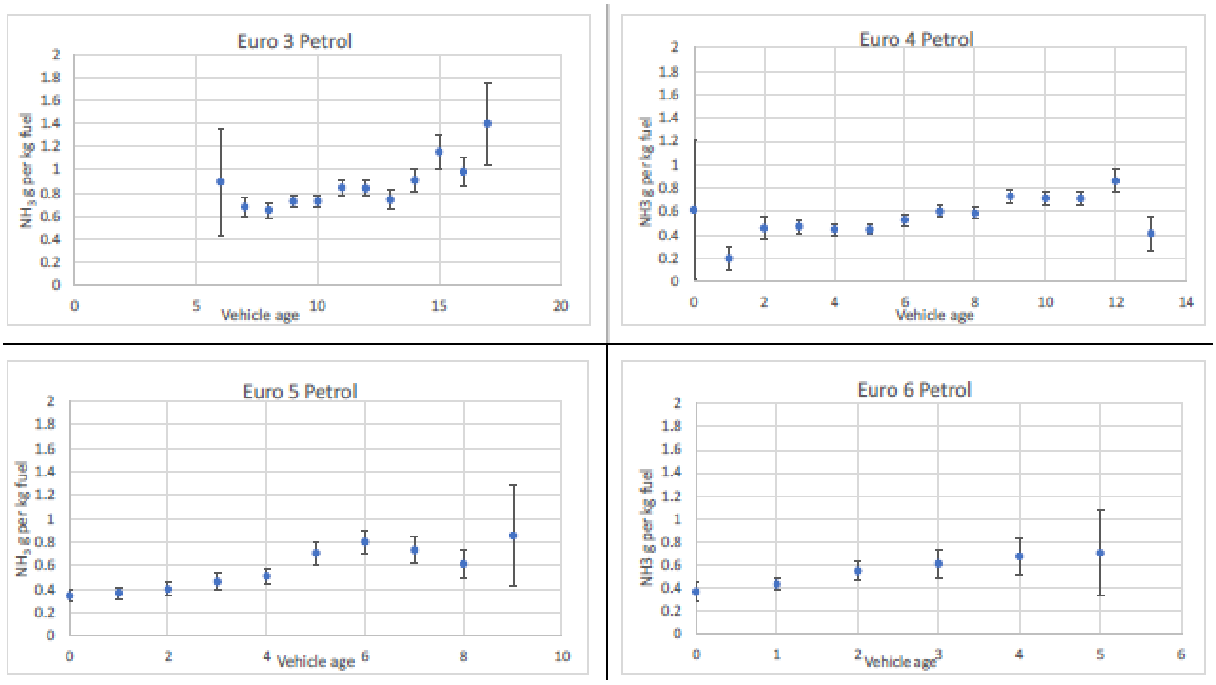

Figure 19. Real-world fuel-specific NH_3 emissions for vehicles divided by Euro class and as a function of vehicle age; image source: [237]

Despite a relatively limited number of exceptions (as mentioned above), the topic of ageing-induced NH_3 selectivity modification appears to have thus far received relatively little attention in the literature. A recent study [232] attributes decreased NH_3 emissions and increased NO_x emissions occurring as a result of TWC ageing to reduced WGS promotion. However, one of the major parameters expected to control both $DeNO_x$ effectiveness and overall system NH_3 selectivity is OSC. OSC is well known to be adversely affected by TWC ageing mechanisms and to generally reduce over time. The impact of reduced OSC on the selectivity towards NH3 formation is frequently mentioned in recent literature on the subject and is this is reviewed and explored in the following section.

3.8.3.TWC oxygen storage capacity (OSC)

The presence of metal oxides in a TWC – in both quantitative and qualitative terms – is a very important determinant of its performance under transient operating conditions, due to the OSC functionality such materials provide. As is well-known, in addition to providing the OSC, these oxides also improve the stability of the noble metals. However, they can also promote certain reactions (i.e. serve as catalysts in their own right), including for reactions relating to the reduction of NO and WGS [241]. Ce is intimately involved in providing OSC and has been shown to play important roles in terms of catalysing reactions which *consume* NH_3, the final products of which can be N_2, NO or N_2O [166]. As a general point, it should be noted that regardless of their origin, the presence of dopants such as transition metals can strongly affect OSC and dynamic adsorption/desorption behaviour for varying temperature and O_2 concentrations [242], [243]. Ageing can induce a variety of highly complex physiochemical effects including modification of bond lengths and significant modification of electrical properties (ionic conductivity) [244], the latter being strongly dependent on the valence state of the dopant [242].

Ageing – both thermal ageing [207], [229], as well as chemical ageing associated with certain elements, including those such as phosphorus which commonly enter a TWC via the lubricant [245], [246] – has the potential to severely affect TWC performance via reduction of the physicochemical viability of mechanisms that provide OSC. In addition to generalised, overall loss of OSC functionality, specific loss of the ability to undergo the relevant OSC reactions on the appropriate timescales and at the relevant range of temperatures leads to observed decreases in TWC effectiveness, particularly for cold start driving cycles of relatively limited duration (e.g. $<10^3$ seconds). Figure 20 shows an example of the aforementioned effects.

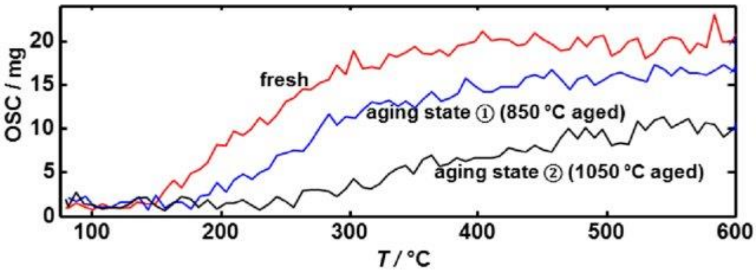

Figure 20. OSC as a function of temperature for a simulated exhaust gas stream with oscillating λ for TWC samples tested at three ageing states (ageing duration for “1” and “2” = 12 hours); image source: [247]

During ageing which occurs under real-world scenarios (including both stoichiometric and non-stoichiometric operation, the latter including frequent fuel cut-off), there is an overall tendency for sintering and surface area loss to occur, leading to marked reductions in OSC [242], [229], [248]. The accumulation of heteroatoms originating mainly from engine oil (and other sources, including fuel, wear and erosion of engine materials and even intake air) acts antagonistically, compounding purely thermal effects and thereby causing significant OSC loss [246], [249]. Ageing equivalent to a few hundred hours of moderate-to-high load operation – a scenario which could easily occur in the first ~2 years of a passenger car’s life – has been reported to cause reductions in OSC on the overall order of 50% [242], [250]. For a cold start driving cycle, significant OSC may become available noticeably later in the cycle if the bound oxygen is available only at higher temperatures [228]. Materials which provide the OSC are also known to play an important role in the reduction of NO, primarily as a strong promotor of the WGS reaction. Thus, the physicochemical state of the metal oxides present in the TWC (support and OSC-promoting materials) could have somewhat counteracting effects on the formation of NH_3 – on the one hand, a reduction in available OSC will lead to more frequent occurrence of reducing conditions within the TWC during periods of operation at $\lambda<1$, due to the decreased oxygen buffering ability; on the other hand, reduced promotion of the WGS reaction would suggest that the magnitude of a reaction closely linked to the formation of NH_3 (a key source of H2) is at least somewhat diminished.

A very strong linear correlation between OSC and NH_3 selectivity has been reported; extended ageing of a TWC has been shown to decrease OSC and thereby increase the NH_3 selectivity from 9.7% to 33.7% (*ceteris paribus*) [235]. The fact that extended periods of non-stoichiometric operation often cause NH_3 surges thus appears to be well correlated with – and fundamentally related to – the finite nature of OSC for a given system. While rich excursions are often unavoidable using current SI ICE technology, controlling the duration of rich excursions so as to prevent total reduction of the OSC is considered a viable strategy to prevent surges of NH_3 [166] and would also have benefits for other pollutants, chiefly CO. The use of so-called dithering is also important in this regard: the mean value of λ measured on longer timescales may appear may appear to be very close to 1.0, but dithering can induce NH_3 formation; as might be excepted in light of the considerations above, low frequency, high amplitude dithering is most conducive to NH_3 formation [251], which supports the argument for limiting the duration of λ excursions.

In terms of considering the general emissions control implications of NH_3 interacting with oxygen, it should be noted that interactions between NH_3 and O_2 do not inevitably result in the formation of NO or NO_2 [166], [252]; if the stoichiometry allows, nitrogen can return to its unfixed form N_2, i.e. by far the most desirable outcome:

$$4\mathrm{NH_3} + 3\mathrm{O_2} \rightarrow 2\mathrm{N_2} + 6\mathrm{H_2O} \tag{11}$$

Less favourably, if slightly more oxygen is available (1:1 molar ratio with NH_3) and the temperature is high enough, the following reaction can occur:

$$2\mathrm{NH_3} + 2\mathrm{O_2} \rightarrow \mathrm{N_2O} + 3\mathrm{H_2O} \tag{12}$$

3.9. The impact of powertrain operation parameters and resulting exhaust gas composition on NH_3 emissions

Plentiful literature exists on the subject of the correlation between engine, powertrain and vehicle operating conditions and gaseous exhaust emissions; indeed the topic is one of the main areas of investigation in modern automotive engineering. However, as the vast majority of these studies focus on regulated emissions (or, more specifically, pollutants which are regulated in at least one jurisdiction), the sub-set of published sources dealing with the subject of NH_3 emissions is relatively small. While publications from a wide range of disciplines may prove informative in investigating the overall phenomenon which is the subject of this thesis, it should be noted that essentially three types of study can be considered useful sources of information on factors affecting the formation of ammonia within a TWC:

- Firstly, studies reporting measurements of the NH_3 released from an engine, powertrain or vehicle being tested in a laboratory or real-world setting are available in the literature, often being published within the field of mechanical/automotive engineering. A notable sub-set of this first category is for measurements performed using portable emissions analysers (PEMS) testing emissions from a vehicle being driven on public roads. Such studies produce data of high relevance to the subject under consideration here, but typically tend to focus on a limited number of vehicles (and sometimes a single vehicle).
- Secondly, many laboratory studies of TWC units using artificial feed gases (idealised synthetic analogues for exhaust gas at a given value of λ) include – or even primarily focus on – the formation of NH_3. Such studies often reside within the literature on applied catalysis and chemical engineering; they often examine chemical phenomena occurring under static or quasi-transient conditions and tend to provide detailed analysis of the chemical reactions, derivation of stoichiometries, rate laws, etc. Such studies provide the most insight into the fundamentals of the NH_3 formation process, yet are self-evidently at least somewhat removed from real world emissions scenarios occurring in road vehicles.
- A third category is that of vehicle remote sensing measurements, where a relatively simple measurement system, often focusing on a limited range of compounds, is used to monitor concentrations of selected gaseous pollutants in the air within the close vicinity of large numbers of moving vehicles. Sample sites may be targeted for the large numbers of vehicles likely to be present, for their isolation/limited ventilation (tunnels), for the predominant driving conditions (e.g. a location where the infrastructure-traffic system is suspected to cause exhaust emissions to be higher than usual), or even for all of the above reasons. Such studies can make use of

devices for measuring speed and acceleration in attempts to link the measured concentration to the vehicle's operating conditions. For certain locations, such as the entry to a car park or similar, the direction in which the vehicle is travelling and/or time of day will be strongly correlated with the thermal state of the powertrain, thus allowing non-invasive determination of that parameter and thus facilitating reasonably robust correlation of measured emissions (e.g. [253]).

While it is often stated in the literature (both technical and popular) that the air:fuel ratio must be precisely stoichiometric in order to achieve high efficiency simultaneous conversion of THC, CO and NOx, there is in fact a range (termed "window") of lambda (λ) values at which three-way conversion effectiveness is deemed to be acceptably high [71], [254]; the very highest overall holistic conversion efficiency values (for THC, NMHC, CO and NO_x) are in fact normally achieved at values slightly < 1. Since two diametrically opposed chemical processes (i.e., oxidation and reduction) are occurring simultaneously within the TWC, the width of the aforementioned window is indeed extremely narrow where the TWC has no facility to store oxygen; the OSC is therefore a critical factor determining TWC performance under conditions which deviate from λ1 [242], [255]. The ability of the TWC to buffer the fluctuating oxygen concentrations inherent in highly transient SI engine operation with sufficient rapidity depends on a range of complex interacting factors [256]. These include the storage capacity itself (the product of the volumetric unit OSC value(s) and the total substrate volume), reaction kinetics and a very strong overall thermal dependency [243]. At higher temperatures (e.g. ~600°C) even large engine-out lambda excursions can be moderated to relatively constant post-TWC λ values, while at lower temperatures (e.g. 200-400°C) the oscillations are reduced in amplitude but remain in evidence [257]. In many cases, such effects may prove to be of high explanatory power in terms of explaining the thermal dependence of NH_3 emissions behaviour observed during cold start driving cycles.

A further consideration to mention here is that it is essentially impossible for a practical combustion engine to operate at precise, perfectly stable λ value of 1 – for multiple reasons. The power demand that results from transient driving is one reason for this, as well as cold start effects, but perfect $\lambda = 1$ is not possible even under thermally stabilised steady-state operation conditions. Inherent oscillations in the air:fuel ratio mean that λ may appear to take a value of precisely 1.0, but this is at least somewhat dependent on the sampling ratio; a low sampling frequency or use of a signal smoothing or even a simple averaging algorithm may thus obscure the full complexity of the picture regarding λ and its inherent instability. It has long been reported that the values taken by λ typically oscillate with a frequency of a few Hz [71], although advances in technology (particularly response time of oxygen sensors and processors' clock speeds) may have increased this characteristic frequency somewhat in recent years. On the other hand, it is significant that the frequency of such oscillations may be considerably lower where dithering is applied as a deliberate emissions control strategy [251], [258], or indeed where it serves as an engineering measure to induce gasoline particulate filter (GPF) regeneration [259]. Furthermore, as shown by Heywood [71], even where the overall value of λ takes an apparent value of 1, the cylinders of multi-cylinder engines will have unequal air:fuel ratios and exhaust gas composition will be richer in O_2 and CO (and poorer in CO_2) than would be inferred from the overall λ value [71]. Inertia caused by turbocharger lag and the dead volume of the EGR system (if such systems are present) and the imperfect actuation of injectors can also contribute to instability in λ. In fact, turbochargers can represent a special case, for other reasons, since the use of the practice known as "scavenging" (where applied) to militate against turbo lag at low load results in significant quantities of excess intake air being admitted, thus causing a situation where $\lambda >> 1$, which is compensated for by over fuelling [260]. Post-oxidation of the charge is a complex phenomenon controlled by many factors [260], [261]; the meeting of oxygen-rich air and a hydrogen-rich mixture and the ensuing chemical reactions have implications for many aspects of the functioning of downstream components (i.e. the TWC(s)) [262],

[263]. Turbocharger concepts with very rapid and dependable response times are considered a means to achieving $\lambda = 1$ engine maps [264]. A further consideration is that non-pristine (e.g. field aged) λ sensors can present slightly slower response times, which has obvious implications for the performance of closed-loop control systems operating under highly transient conditions.

TWC temperature and exhaust gas composition

The temperatures of various powertrain elements are of paramount importance in analysing and parametrising a wide range of emissions behaviours. In the specific case of TWC-facilitated formation of ammonia, the temperature of the TWC is of far greater importance than the temperature of other powertrain elements. That being said, the relationship between powertrain temperatures and engine-out emissions is also of note in this context, as the concentrations of the various feedstocks for production of ammonia with the TWC are linked to various temperatures.

For a TWC, the temperatures of interest are the points at which the intended reactions begin to occur at significant rates within the TWC. This means the temperature (or temperatures) at which the conversion of regulated pollutants THC, CO and NO_x into CO_2, H_2O and N_2. As conversion effectiveness generally follows a sigmoidal curve, whereby activity is essentially nil at “low” temperatures, rising swiftly before forming a plateaux at some “high” temperature, the point normally used as a reference temperature is the T50 value. As has been noted in certain detailed studies (e.g. [265]), the effectiveness of NO conversion is not fully monotonic with increasing temperature (*ceteris paribus*) and the ΔT between T50 and T90 can be surprisingly large (~150°C), although there is great sensitivity to λ, with NO T90 increasing very rapidly with increasing λ where $\lambda > 0.995$, but being essentially unaffected by λ where $\lambda < 0.995$ [265].

It is noteworthy that any cold start emissions test conducted on a modern vehicle with an SI engine employing a driving cycle covering some normal distance (> 5 km, say) is in effect studying the emissions behaviour under three regimes: the cold start event; the TWC warmup and light off period; and finally hot running conditions. In terms of the fundamental link between TWC temperature and the formation of NH_3, an obvious choice for reference temperature is the NO_x T50 (although NO T50 is more commonly encountered in the literature). This value varies from system to system, but is not fixed for a given system, since it varies with the composition of the feed gas. It is normally at least somewhat lower than the corresponding temperature for CO and is always much lower than the temperatures required for oxidation of various hydrocarbons and most organic molecules. The NO light-off temperature is highly sensitive to λ – to a much greater extent than for the cases of CO and many hydrocarbons [266], [267]. At most normal operating conditions for SI engines, the NO_x T50 of a TWC normally lies at a value of slightly over 200°C (~475 K), although this can be lower, depending on the formulation; in line with the aforementioned λ dependence, the level of available oxygen has a significant impact, with lower O_2 levels mixtures causing NO light off at significantly lower temperatures [265], as indeed normally occur immediately following cold start. Under light-off conditions, i.e. for temperatures within the region of NO T50, the actual state of the Pd surface within a TWC has been reported to be significantly more reducing than would be implied by the oxygen content of the feed gas [268], which might aid explanations of the high propensity for NH_3 formation around light-off, even where mixtures are not particularly fuel-rich (see the following section for further discussion).

Some measurements appear to show the release of NH_3 from a vehicle’s tailpipe well before NO T50 can have been reached, (e.g. [7], [132], [269]), but this may in fact be a manifestation of outgassing of latent ammonia from the metal surfaces of the exhaust line, although outgassing of stored NH_3 ought to be limited at such low temperatures.

Experimental investigations into the precise relationship between TWC temperature and NH_3 formation can be found in the literature. One of the first studies to investigate this point in detail was published in 2005 by Heeb et al. [270], who performed detailed investigations and reported a non-linear but proportional dependency between TWC temperature and NH_3 formation. These studies were performed at the vehicle level and thus temperature is not the only variable, as the temperature essentially resulted from the engine operating points dictated by the driving profile, which simultaneously changes in terms of the exhaust gas flow rate (i.e. TWC space velocity), λ, etc. Significantly, the selectivity for NH_3 formation was found to be highest within a relatively narrow thermal range, of which the lower boundary was assumed to be the NO T50 and the upper boundary was reported as ~300°C. Selectivity towards NH_3 formation was significantly reduced above this upper boundary temperature, thus reinforcing the notion that NH_3 production is mainly associated with TWC light off and that hot-running emissions are of a lower magnitude. Indeed, setting aside, storage and release effects, many vehicles show similar behaviour when tested over a cold start driving cycle: a surge of ammonia formation occurs relatively early in the cycle, broadly corresponding to TWC light off – more specifically, to NO light off – and later portions of the cycle often show relatively limited NH_3 emissions, even where other parameters (such as λ and engine-out NO_x emissions) might appear to be conducive to NH_3 formation. Note that such a hypothesis would suggest that if the time taken to reach the NO T50 is longer, the initial NH_3 surge should occur somewhat later as a result.

A thorough review carried out in 1980 [271] revealed that the consensus among studies conducted up to that point was as follows: below 350°C selectivity towards N_2O is the highest; between 300°C and 600°C selectivity towards NH_3 is generally high, reaching a peak somewhere within that range; at higher temperatures N_2 is the dominant product. Generally speaking, the transitional behaviour observed during cold start driving cycles follows the scheme described above, although storage and release effects, apparent sample loss, the specifics of the driving trace and various anisotropic effects can complicate matters. An experimental study conducted in 2012 [272] reported very similar results:

> *"N_2O is observed primarily [at] 110–320°C;*
> *NH_3 is formed in the 200–600°C range".*

However, such findings conflict somewhat with those reported by others [270], which state that above 300°C selectivity towards NH_3 was found to be very low. A recent study [273] found that the concentration of NH_3 was highest within the range 550–625°C, being significantly lower outside that range, even for relatively high load operation. In interpreting these apparent discrepancies, it is worth recalling that investigations of a given system or a small number of systems (whether commercially available or not) always carry the risk of producing somewhat system-specific results.

The existence of an NH_3 "thermal window" (see e.g. [273]) is a concept of potentially high explanatory power in terms of explaining unexpectedly low NH_3 emissions from driving patterns which, based on consideration of factors other than temperature, might be expected to produce high NH_3 emissions. In concise form, it may be generally stated that under many driving conditions the TWC may be at too high a temperature to produce NH_3 at the levels expected, thus concentrating emissions in the cold start/warmup phases. Physicochemical explanations for the reduced selectivity towards NH_3 at higher temperatures are of two varieties: firstly, arguments that formation of NH_3 becomes thermodynamically unfavourable, or secondly that formation continues, but that NH_3 is *consumed* in a reaction which occurs before it leaves the TWC. As regards the first effect, various explanations have been offered, including the fact that at higher temperatures hydrogen preferentially reacts with oxygen [274], although the limited availability of O_2 during prolonged rich excursions and the highly reducing environment caused by very high levels of CO and H_2 mean that there are certain conditions under which this effect would not be expected to occur. As regards the second effect, substantial experimental evidence for near-simultaneous NH_3 production and destruction (either via thermolysis of NH_3 to N_2 and H_2 [166], or via consumption of NH_3 molecules in other reactions, involving NO and/or O_2 [275]) within TWCs was already clear in the early 1980s [271] and has since been confirmed [166]. Even in the absence of significant levels of free (gaseous) oxygen, oxygen stored on ceria can facilitate oxidation of NH_3 until such time as the OSC is mostly depleted (and later fully depleted) [166]; OSC-based reactions are well known to be strongly dependent on temperature. Where reactions with O_2 can no longer occur due to a lack of availability, the main remaining viable mechanism to explain the apparent disappearance of NH_3 from the exhaust gas stream is decomposition via thermolysis. Note that the exact same phenomenon – final emissions being determined by the balance resulting from the net difference in formation and destruction occurring within the TWC(s) – is also mentioned in the context of N_2O emissions [276].

When considering the engine-TWC system, no parameter (perhaps other than whether the temperature of the TWC is above its light off point) is as important as the instantaneous air:fuel ratio, commonly called ‘lambda’ and denoted by the Greek letter λ. Formally, λ is defined as the instantaneous value of the mass-based ratio of air to fuel for the combustion cycle currently in progress divided by the stoichiometric value for that ratio, based on the oxygen demand of the fuel type in use and the volumetric proportion of oxygen in the intake air. Since the oxygen demand of the fuel in use can be assumed to be constant, λ thus represents the presence (or absence) of excess fuel or excess air in the mixture formed within the cylinder. A λ value of exactly 1 represents perfect stoichiometry; lower values represent fuel-rich mixtures and higher values represent fuel-poor mixtures. Note however, that a mixture at a λ value of precisely 1.0 – and even a slightly rich mixtures – still have a certain quantity of oxygen present in the exhaust gas, due to imperfect combustion inefficiency meaning that not all the available oxygen is consumed.

The very strong link between λ and NH_3 formation is noted in virtually every publication on the subject[8]. As explained in this section (and in other sections), this is explainable in terms of a variety of chemical mechanisms, ranging in nature from reagent supply (cf. the 5:2 H_2:NO ratio mentioned previously), to chemical effects such as oxygen suppression of reduction reactions, the favourability of various reactions (which may be conceptualised as separate units in this context – i.e. the reduction of NO, WGS, SR, as well as NH_3 formation – and indeed decomposition). Somewhat more fundamental physicochemical factors, including competition for the finite number of available surface sites and steric effects have also been identified as relevant factors determining variable nitrogen selectivity [106], [216].

In practical terms, for studies conducted at the vehicle or powertrain level, it is often complex to separate the impacts of temperature from those of λ and indeed space velocity, since high space velocities and high temperatures share certain underlying causes with λ (engine load, instantaneous fuel consumption) and can thus coincide. However, detailed laboratory studies focusing on the TWC (or some equivalent thereof) are able to separate out the effects of air:fuel ratio and temperature – an example is shown in Figure 21.

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[8] Note that many studies imply this via the use of equivalent terminology such as “rich”, “excess fuelling”, etc. This is especially true of studies with a non-automotive slant, focusing on air quality, ambient monitoring and source apportionment, where terms such as “during accelerations” and “at high load” may be found. Applied catalysis studies often use vocabulary such as “strongly reducing conditions”, or similar.

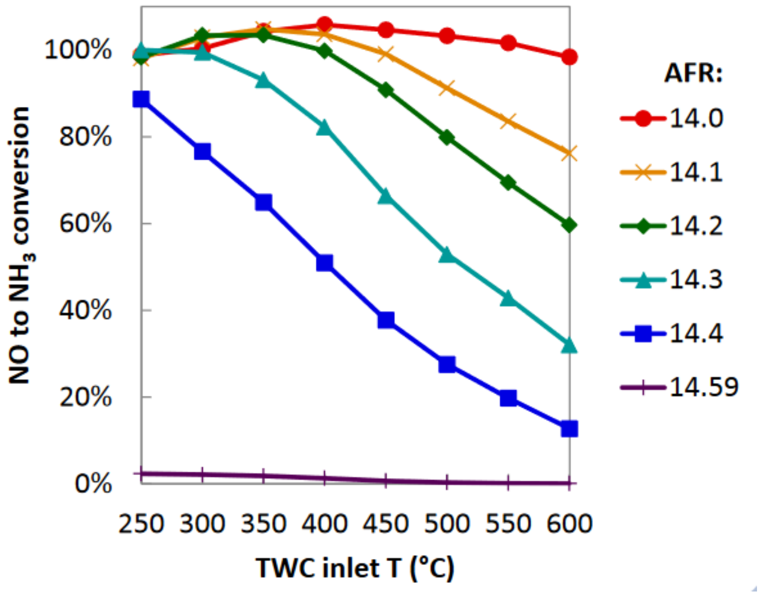

Figure 21. Image source Note: AFR – air:fuel ratio; image source: [222]

Regarding Figure 21, the existence of some reported NH_3 conversion efficiency datapoints taking values > 100% can most likely be attributed to measurement uncertainty and general experimental error (as well as to possible NH_3 storage and release effects).

As previously mentioned, it has been known for decades that efficient simultaneous elimination of THC, CO and NO_x in a TWC presupposes that λ take values of very close to 1 [258], [71]. In practice, this is not always achievable, for multiple reasons. Firstly, for most spark ignited engine designs using liquid fuels, maximum engine power is achieved with a mixture significantly richer than stoichiometric [277]. Excess fuel not only puts the amount of fuel available for combustion into excess, but also significantly cools the charge and increases knock resistance [71]. Secondly, to ensure drivability and stable engine operation, commanded enrichment is used during and following cold start. This is due to the difficulty in maintaining stable combustion when significant amounts of fuel condense on cold surfaces and then evaporate in a stochastic manner, subject meanwhile to highly variable parameters such as the through flow of air (and indeed further fuel). The storage and release of fuel from said surfaces and variable power demand (causing highly variable fuel flow and gas throughflow) also makes the air:fuel ratio very difficult to correct in real time, even with the aid of modern microprocessors. Thirdly, the available enthalpy of vaporisation of liquid hydrocarbon fuel (approaching 0.5 kJ/g; with somewhat higher values for fuel blends containing appreciable quantities of alcohol such as ethanol or methanol) means that the addition of additional fuel has the impact of reducing the peak temperatures achieved in the combustion reaction – this technique is known as [*enrichment for*] *component protection* and is a common approach adopted in engine control strategies [278], [279], [280]. As an overall generalisation, this technique is resorted to much more often in engines of lower displacement and in vehicles with lower power to mass ratios [281], thus somewhat counterintuitively reducing the environmental performance of such units compared to their larger counterparts, from this particular point of view. Specifically, heavily downsized, highly boosted engines are especially reliant on this strategy, since periods of high power demand are met with high levels of boost, which not only creates heat, but also creates a resulting need to protect not only the engine and aftertreatment, but also the turbocharger from thermal damage. Such cooling can often only be provided with the demanded rapidity via the use of excess fuelling to absorb heat and induce knock resistance.

Enrichment can lead to CO breakthrough, i.e. a sudden increase in the concentration of CO downstream of the TWC. This fact is highly significant, since multiple authors report that high tailpipe CO emissions from SI engines resulting from fuel-rich engine operation are often accompanied by emissions of NH_3 on the condition that the TWC's temperature is > NO T50 [50], [58], [85], [282], [283], [284]. The aforementioned observation has been noted repeatedly in the context of emissions from vehicles of varying characteristics, spanning a period of around 20 years, but which also includes vehicles meeting the very latest Euro standards [136]. Indeed, a simple metric based on the instantaneous quotient of CO to (CO + CO_2) showed high predictive power for instantaneous NH_3 emissions [235]. There is also evidence that CO counteracts the inhibiting effect of O_2 on NH_3 formation in a TWC [274]; recall that O_2 remains present in appreciable quantities even at λ values < 1 (O_2 is still detectable in exhaust gas at $\lambda = 0.96$). In the aforementioned studies – and indeed in most contexts – where CO emissions are mentioned as being relevant to NH_3 emissions, it can be assumed that authors are referring to tailpipe (post-TWC) emissions of CO. Few studies make direct comparisons of pre-TWC CO with NH_3 emissions, although a significant correlation between precisely those two emissions has been reported, with $R^2 = 0.75$ [285]. Studies reporting the relationship between post-TWC NH_3 and pre-/post-TWC CO (e.g. [134]) are therefore of greater utility. Breakthrough of CO is indicative of a lack of oxygen and strongly reducing conditions, which, as discussed previously are precisely the conditions which strongly favour NH_3 formation[9].

Another consideration is the fact that hydrogen is rarely measured in ICE exhaust gas, whereas CO is a regulated pollutant, very commonly subject to emissions measurement, often at high temporal resolution. Some authors report that certain engine operating conditions are characterised by low NH_3 emissions due to low availability of CO; however, the phenomenon being referred to might more accurately be described as exhaust gas with $\lambda \geq 1$. Vehicle-level studies correlating H_2 with NH_3 are very scarce – [117] stands out as a rare example, which reported significant post-TWC H_2 emissions. In the same study, H_2 emissions were reported to correlate to some degree with NH_3 emissions, thus confirming that high availability of H_2 causes increased NH_3 formation, but since the data reported post-TWC H_2 concentrations, it is clear that said H_2 was not consumed in its entirety within the TWC.

Notwithstanding the fact that enrichment is very commonly used, there is now pressure to reduce enrichment during operation of SI engines for a range of reasons, ranging from emissions compliance to fuel economy. Simply eliminating enrichment from the ICE's control strategy will lead to unacceptable drivability and carries a risk of component damage (most notably to the TWC and turbocharger), as well as significant power loss [281]. Various strategies have been investigated (and remain under investigation), including system changes to increase thermal tolerance permitting higher temperatures [281] and on-demand injection of water [286], [287], [288], [289], [290].

A final point to consider in the context of the present discussions regards the mathematical significance of inhomogeneity of mixtures which are operating at very close to $\lambda 1$ [71]. Because of this phenomenon, whereby the mixture might appear to be perfectly stoichiometric, but is in fact at $\lambda < 1$ at least some of the time, pulses of rich exhaust gas can pass through the TWC, potentially leading to the periodic formation and emission of NH_3, despite the fact that measurable NH_3 emissions might not be expected based on the measured (or calculated) λ value.

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[9] In this context, emissions of CO can be a parameter of interest in estimating NH_3 emissions from a test where NH_3 was not measured. Excluding cold start events, the breakthrough of CO is associated with λ excursions, especially those of longer duration – precisely the same situation as with formation of NH_3. Thus, substantial CO emissions in the absence of NO_x emissions can be used as an identifier of periods of powertrain operation likely to cause appreciable NH_3 emissions.

3.10. The impact of vehicle operation parameters

3.10.1. Consideration of driving cycles

The previous sections have focused mainly on so-called bottom-up factors. Here, the so-called top-down link between vehicle operation patterns (commonly referred to as a driving cycle, although the two are not fully synonymous) and NH_3 formation and emission are examined. Any closely defined vehicle or powertrain test procedure may be mapped to a set of vectors such as engine rotational speed, demanded torque, quantity of fuel injected per stroke, etc, and ultimately such parameters control the combustion and pollutant formation and emissions processes, as well as the behaviour of the aftertreatment system. However, many studies performed in the automotive industry are highly empire in nature, imposing a top-down regime of powertrain operating conditions as imposed by the chosen test procedure. Two of the most important aspects of the test procedure (for vehicle-level testing) are the driving cycle and the thermal condition of the powertrain at test start, although other factors such as road load simulation, use of the gearbox etc also determine final exhaust emissions.

Worldwide, there are a number of recognised, published driving cycles in use for the type approval of LD road vehicles. As is the case in many branches of modern industry, the automotive industry is strongly guided by type approval requirements. In the field of exhaust emissions research, there is a very strong correlation between formal type approval requirements regarding emissions and widely-used vehicle R&D process. Legislative driving cycles are thus used in the automotive industry for comparative purposes, as well as validation, screening, quality control, continuous improvement, etc. In order for studies to be comparable and reproducible, most authors of published works chose well-known driving cycles; where some exotic cycle is employed, authors typically also test over at least one well-known driving cycle, the latter serving as a useful reference point.

For the years 2000-2017, the NEDC was the legislative cycle used in Europe, for quantification of regulated emissions and fuel consumption/CO_2. Although the term NEDC strictly refers only to the driving *cycle*, the term is often used to describe the entire associated test procedure, which includes road load determination and matching, vehicle preconditioning and measurement of regulated emissions. The oft-noted and widely discussed shortcomings of the cycle itself and the wider test procedure [149] caused it to be replaced in the EU by the WLTC cycle (and, more broadly, by the WLTP procedure) from 2017 onwards, with a gradual expansion of the procedure to the rest of the world (firstly India, China, Japan, as well as some others) currently underway.

In the USA, the FTP-75 cycle serves as the base emissions cycle, complemented by several other cycles, all of which have legal status (i.e. are required for type approval). Of particular interest in the case of hot-running NH_3 emissions – widely recognised as correlating with engine load and especially enrichment during periods of high load – is the US06 test cycle, an extremely demanding driving cycle which requires a vehicle power-to weight ratio in the region of ~140 W/kg (or greater) in order for the speed trace to be followed within the prescribed tolerances.

All of the aforementioned driving cycles consist of a wide range of operating points, sometimes ranging from idle (vehicle standstill) to harsh accelerations and high speed driving and even full load, comparisons and correlations can be made not only between cycles, but also within cycles. This section will mix both approaches.

The literature is for the most part unanimous on the finding that more demanding driving cycles lead to more extensive TWC-facilitated NH_3 production and this higher NH_3 emissions. As a leading example, Durbin et al. [113] stated the following:

> *"NH_3 emission levels increased significantly for the more aggressive US06, NYCC, and high speed freeway cycles. This is consistent with previous studies that have shown increases in NH_3 emissions during periods of richer [engine] operation."*

A further publication published by a group of authors including some of the authors of the [113] stated the following [291]:

> *"…NH_3 emissions are cycle-dependent, with higher emissions found for more aggressive cycles. Modal emissions data show that NH_3 emissions are primarily generated during acceleration events […] Strong correlations were found between tailpipe NH_3 measurements and both vehicle specific power (VSP) and engine-out carbon monoxide (CO) emissions."*

In order to formalise and quantify this postulation, a useful concept from the literature may be used: vehicle specific power (VSP). Developed in the late 1990s [292], VSP is defined as tractive power per unit vehicle mass. The metric normally takes units [kW/tonne], equivalent to [W/kg], expressed in fundamental SI base units as [m^2/s^3]. While the units would suggest that VSP is merely the speed·acceleration product, the VSP metric includes other factors and the correlation between instantaneous CO, HC, and NO_x emissions and VSP was reported to be stronger than when using other instantaneous metrics such as such as speed, acceleration, the speed·acceleration product, instantaneous engine power, or fuel flow rate [292]. Following the initial application of this technique in the case of ammonia [285], [293], other authors have followed this approach in their studies of NH_3 emissions and over 20 years after it was first defined, the technique remains in general use in a wide range of automotive emissions contexts (e.g. [294], [295]). A key finding, oft-repeated and independently confirmed (e.g. [182]), is that higher VSP values tend to cause higher NH_3 emissions. As has been widely noted in the literature for many years (e.g. [118], [270]), other metrics which correlate with VSP, such as the speed·acceleration product, or the 95th percentile thereof, also tend to show a reasonable correlation with NH_3 concentrations and gravimetric emissions [135], as shown in Figure 22.

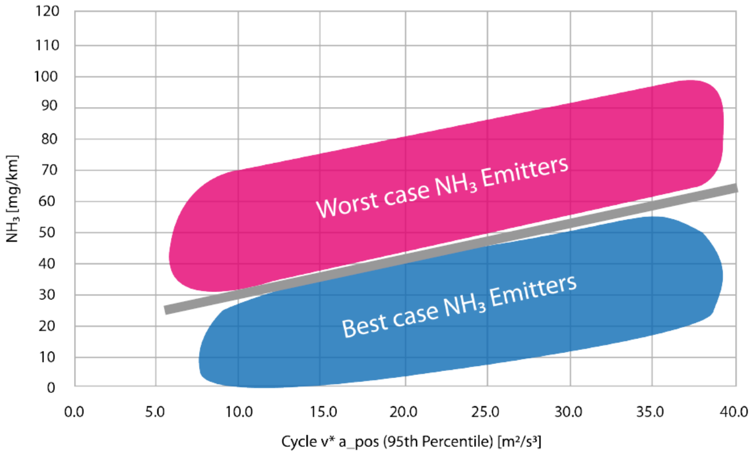

Figure 22. Summary of the relationship between cycle aggressiveness (quantified as the 95th percentile of the product of velocity and positive acceleration and distance-specific gravimetric NH_3 emissions obtained from multiple vehicles tested over multiple test cycles at multiple ambient temperatures. The

results have been generalised and divided into 2 groups, with the line dividing the two groups representing a reasonable proxy for the average case (grey line added by author). As a reference point, the v·a_pos95 value for the WLTC is approximately 14 m^2s^{-3}, while for the NEDC the equivalent value is approximately 8 m2s-3; for RDE-compliant motorway driving, values may approach a value of 30 m^2s^{-3}. Image source: [135]

3.10.2. A note on the "crescendo effect"

A common feature of many driving cycles and vehicle testing procedures is that they tend to commence with lower speed driving and the maximum values of vehicle speed, demanded wheel work, engine power, etc tend to occur relatively late in the cycle. The author tentatively offers the term *crescendo* to describe this effect. In this way, the cumulative mean speed tends to increase quasi-monotonically during the course of the test procedure. This can have important implications for emissions behaviour, especially for cold-start driving cycles. The WLTC, NEDC and the EU's RDE test procedures all require driving of this type, i.e. a cold start, followed by relatively gentle urban driving, followed by higher speed, driving, with speeds >100 km/h occurring in the final sections of the test, yet real-world driving scenarios deviating from this template are self-evidently possible. This topic is returned to later in this thesis, in the context of analysing experimental work carried out by the author.

4. The quantification of NH_3 emissions in the automotive context

4.1. Initial comments

This section aims to provide a brief synthesis of knowledge on the topic of quantification of ammonia emissions in the automotive context, based on an examination of the literature, as well as the author's experience in conducting experimental work on the subject. As is explored in this section, the case of NH_3 is somewhat different from many other pollutants measured in the automotive context, due to certain characteristic properties of the ammonia molecule, as well as the fact that exhaust gas concentrations can cover a very large range of concentrations, since NH_3 does not originate in the combustion reaction (unlike in the case of virtually all other pollutants emitted by SI ICE-based powertrains).

4.2. Analyser types for the quantification of NH_3 concentrations in a gaseous medium

As the following section will focus on the practicalities of measuring ammonia emissions in the specific application of vehicular exhaust emissions testing, this section will focus on the quantification of ammonia concentrations via analysers, rather than the sampling specifics.

Ammonia can be quantified from gaseous samples via a wide range of techniques [296], including those used in analytical chemistry [297], optical methods (discussed below) and various solid state technologies [298]. Overall, there are four well-known types of physicochemical processes which can be used to quantify ammonia concentrations: Fourier transform infrared (FTIR) spectroscopy; quantum cascade laser (QCL) infrared spectroscopy; chemiluminescence and photoacoustic spectroscopy. These techniques are briefly described and their relative advantages explored in the remainder of this section.

FTIR spectroscopy is a technique which was developed in the 1950s and has been employed in automotive contexts since at least the mid-1990s. Based on the use of electromagnetic radiation residing in the infrared range (but making use of more than one wavelength) to interrogate the gaseous sample, it is a technique with high post-processing requirements, but one which has the advantage that a the concentrations of a very wide range of compounds can be measured simultaneously. A well-defined infrared spectrum is defined for NH_3 and commercially available FTIR analysers (for use in a range of fields) routinely advertise their ability to quantify the concentration of NH_3 in the sample gas. Scans are often performed at a high frequency and results are typically available at 1, 5 or even 10 Hz. FTIR response time is typically sufficiently fast for automotive applications: t_{10}–t_{90} in < 1 sec – however, the flow rate of the sample gas needs to be of an adequate magnitude in order to ensure acceptable performance. The availability of simultaneous measurements of other compounds, including the other RNCs and other species possibly of interest, such as isocyanic acid, nitric acid) as well as the main NH_3 precursor molecules (except H_2, which cannot be measured via FTIR) can provide significant additional insight into the dynamic NH_3 formation mechanisms occurring during engine/vehicle operation.

Laser-based spectroscopy relies on the use of high-efficiency lasers operating in the mid-infrared region. Such analysers may or may not make use of quantum cascade technology (QCL). The 'quantum' and 'cascade' components of the technology's appellation refer, respectively, to the quantum tunnelling of photons between wavelength bands and the use of a mechanism where weak initial signals (i.e. those resulting from low concentrations) are magnified in a cascading effect which amplifies the initial excitation and thus derives a sufficiently strong final signal from a weak initial signal. Depending on analyser design (both in terms of hardware and software), the list of compounds whose concentrations can be quantified via this technique is relatively long. Specifically, all four RNCs can be measured this way, in a direct fashion and with minimum interference. Certain hydrocarbons, organic molecules and even CO/CO_2 can also be measured, yet in automotive applications the analyser's list of analyte(s) is normally restricted to one, two, three or all four of the RNCs. The aforementioned signal multiplication effect means that very low concentrations of the compounds of interest can be measured.

Chemiluminescent methods involve detection of the optical radiation emitted by NO_2 molecules undergoing a reaction. Where NH_3 is the compound of interest, the measurement method is thus indirect. Separate sample gas streams are subjected to different treatments – crucially, including a catalyst which converts NH_3. The difference in the measured concentrations for the streams which have/have not been catalytically treated is equal to the concentration of NH_3 in the untreated sample gas. Chemiluminescent technology itself is well established in many fields, including in the automotive industry, for the quantification of NO_x (an application in which its name is often shortened to CLD). In such an application, the reaction between NO and ozone emits light of a characteristic wavelength. It is worth noting that there is the potential for NH_3 to complicate and confound NOx measurements via CLD, as well as to lead to modifications of the activity of catalytic systems for selective stream preparation [299]. Indeed, it is reasonable to assume that a small fraction of the NO_x quantified via analysis of diluted exhaust gas from vehicles with SI engines was in fact emitted as NH_3 – and not as NO, nor NO_2. Simplified systems employing sensors (rather than full analysers) are much more prone to this problem [300], [301] – the literature contains an example of a simple correction algorithm to counteract this tendency, whereby all NO_x detected for instantaneous operating points where $\lambda<1$ was assumed to in fact represent the presence of NH_3 molecules (and not NO_x) [183].

Photoacoustic methods, which may be implemented making use of QCL phenomena, involve microphone detection of the acoustic signal (pressure wave) generated by the molecule of interest (i.e. NH_3, as well as N_2O in some cases) upon absorbing modulated optical radiation. A potential limitation here is that sample heating in the pre-treatment process can confound the measurement somewhat – the microphone signal can be affected by the "noise" created by high temperature gas molecules. Certain systems use internal dilution to overcome this problem, which puts them in opposition to most other commonly used analyser types used for quantification of NH_3, where no sample dilution is used. Alternative methods are also available, making use of techniques employed in analytical chemistry [115]. The vast majority of such techniques are applicable to discrete, non-instantaneous ("batch") sampling.

A recent discussion of the main methods of quantification and an inter-comparison of results is available [7]. In terms of legislative requirements, the EU's Euro VI HD requirements permit the use of a laser diode spectrometer-based analyser (with or without QCL), or an FTIR analyser for quantification of the concentration of NH_3. Arguably the most important trend in emissions control in recent years has been that of demonstration of compliance outside the laboratory, i.e. under real-world conditions. It has been demonstrated in multiple experimental campaigns that NH3 emissions could be measured using mobile testing apparatus under RDE test conditions, irrespective of the vehicle's size, type or fuel type [302], [303], [304], [305]. At the time of writing, the literature consensus is that the leading technology for robust, dependable mobile measurements of NH_3 in the RDE context is FTIR [83].

4.3. Requirements for analysers for the quantification of ammonia

The question of analyser range and rapidity of response is an important point which can determine the accuracy of real-time measurements of any chemical species. It should be noted that it is extremely unlikely that an analyser designed for measuring ammonia is ambient air will be able to provide satisfactory measurements of ammonia in exhaust gas (or vice-versa) due to the massive disparity in the concentration (around 3-4 orders of magnitude) in each case. Measurement of ammonia in ambient air presents numerous challenges [306], some of which are shared with measurements in the automotive context. In particular, problems associated with the high “stickiness” of the ammonia molecule appears to be a significant problem in all types of NH_3 measurement [307]. (This topic is discussed in detail in the following section.)

In the context of emissions from TWC-equipped vehicles, it should be noted that for most vehicles, for a relatively high proportion of the time the concentration of NH_3 in the exhaust gas will be low. The 10th percentile of NH_3 concentrations measured for some modern SI vehicles can be as low as 1–2 ppm, even for cold start driving cycles, while the 100th percentile can take relatively high values (often $\geq$ 500 ppm). Establishing any kind of baseline level of the NH_3 concentration is highly problematic, because of different vehicles’ response to a given duty cycle, as well as variations in TWC chemistry, state of degradation, etc. Nevertheless, the majority of vehicles will have periods where the NH_3 concentration is essentially zero ppm and thus the lower limit of detection of the analyser is of relevance in considering the statistical validity of measurements. As mentioned previously, ambient concentrations of ammonia are generally low; any ammonia entering the engine is likely to be oxidised in the combustion reaction; formation of NH_3 within the cylinder during the combustion process is extremely limited; there are certain conditions where the formation of NH_3 in the TWC is not favoured in terms of thermodynamics and the pure availability of the required feedstock gases, for example during fuel cut-off. As such, it is clear that for TWC-equipped SI vehicles there will be periods of essentially zero emission of NH_3. A further consideration here is storage and release effects, which have the overall tendency of reducing the maximum measured concentration and increasing the mean measured concentration (*ceteris paribus*). At the other end of the scale, the maximum concentration is also rather hard to determine with any accuracy. Since all viable reactions for formation of NH_3 involve NO_x as a reagent, the concentration of NO_x in the exhaust gas entering the TWC would appear to be a reasonable proxy for the upper limit of the NH_3 concentration of gas leaving the TWC (excluding any storage and release effects). Indeed NH_3 yields of ~100% (i.e. full conversion of NO_x to NH_3) have been reported for certain TWCs under certain conditions [222]. While NH_3 concentrations exceeding 1000 ppm can indeed be found in the literature, results from the literature overwhelmingly do not appear to include concentrations exceeding a level of ~1500 ppm and the highest result found – a clear outlier – was approximately 1950 ppm [222]. As such, the range of concentrations deemed likely to occur would span the range from essentially 0 ppm to around ~1500 ppm, with the probability of the occurrence of higher concentrations falling sharply.

Accurate measurement of very low levels of NH_3 may simply not be possible with an automotive NH_3 analyser which has previously experienced significant exposure to higher NH_3 concentrations, due to storage and release effects – extended purging of the sampling system and the analyser itself and possibly replacement of filter(s) would prove necessary in order to achieve satisfactory performance. Purging with N_2 may appear to be an attractive strategy, but in fact untreated ambient air is highly effective as a purge gas (as it contains very low levels of NH_3 and significant quantities of water vapour) [308]. When sampling well-mixed ambient air, automotive NH_3 analysers typically report fluctuating concentrations which are not statistically distinguishable from 0 ppm, as the true ambient level is <<1 ppm, which represents a very small fraction of the full range of the analyser. Because of the aforementioned factors, it is not necessary (nor technically feasible) to perform any kind of background correction for NH_3 concentrations (as commonly performed for diluted and undiluted measurements of concentrations of CO_2, NO_x, etc.). However, measurement of background levels is an important plausibility check to be performed before testing commences.

In addition to the range defined for measurement (and thus calibration), the analyser response time is of significance in determining the suitability of a given device or detection method for measuring concentrations of NH_3. As previously mentioned, concentrations at a level of 0 ppm are to be expected, as well as concentrations of several hundred ppm (and potentially even higher). The strong correlation with lambda and the generally highly transient conditions under which SI engines used in road transport operate mean that the minimum and maximum concentrations measured during an emissions test could potentially occur very close to each other – i.e. a step change from a very low values to highest value measured during the test could occur within the course of a few seconds. The time taken to respond to such rapid changes can be measured experimentally and is normally guaranteed by manufacturers of specialised analysers, not least because EU HD legislation [309] contains a requirement that rise time of the NH_3 analyser shall be ≤ 5 s[10]. Analysers invariably feature a filter of some kind to prevent the ingress of soot etc into the analyser itself. As the quantity of soot, heavier hydrocarbons, etc on the filter increases during normal usage, this can noticeably affect the sample transport delay time. For a reactive, hydrophilic molecule like ammonia, this effect is expected to be stronger than in the case of other species.

4.4. Problems associated with the measurement of ammonia in automotive contexts

This discussion will be limited to discussion of the problems and practical challenges posed by measurement of exhaust emissions of ammonia in laboratory contexts. As vehicle-level testing in a laboratory context is conducted on chassis dynamometers, this will be the experimental setup assumed in these discussions. Note, however, that some of the challenges for measuring ammonia on an engine dynamometer are similar or identical to the challenges discussed here. Measurement of NH_3 emissions from passenger cars (as well as other road transport applications for which SI engines are used, such as mid-sized vans and motorcycles) under real-world operating conditions (i.e. outside the laboratory, on public roads) will be discussed briefly at the end of the section.

In terms of problems and challenges to be overcome when measuring ammonia in the automotive context, the most significant problems arise from a single fact: the stickiness of the ammonia molecule. Formally defined as a strong tendency to adsorb onto the surfaces of certain materials, this fundamental property of ammonia creates oft-commented difficulties regarding its measurement. The term has been used in the literature in recent years when discussing the measurement of NH_3 and in fact usage of the term in this context has occurred in contexts not limited to automotive exhaust gas measurements (e.g. [34], [296]). The result of this behaviour is that NH_3 molecules can adhere to hard surfaces with which they come into contact, remaining on the surface for a non-trivial time (i.e. long enough to affect measurements). Any analyser designed for the quantification of NH_3 concentrations must be constructed in such a way that all parts which come into contact with the sample gas are made of materials proven to have as low a propensity as possible to enter into physicochemical reactions with all exhaust gas components including NH_3. These reactions are chiefly (but not exclusively) adsorption. The conversion of NH_3 to some other species before it can be measured is also a relevant concern, but in such cases the materials used to convey the sample gas are of low relevance, as such reactions occur as a result of interactions between NH_3 and other gaseous components already in the exhaust gas, mainly water and NO_x. The connection to the transfer tube connected to the vehicle's exhaust pipe should be as short as possible and opportunities for gas-metal contact should be kept to an absolute minimum. A sample transfer line consisting of Teflon™ tubing housed within a heated jacket is an optimal solution, leading

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[10] "Rise time" is defined as follows: "…the difference in time between the 10 per cent and 90 per cent response of the final reading (T90–T10)."

to low sample loss. The temperature of the heated line should be significantly greater than 100°C to avoid problems with condensation of water; an expected co-benefit here is that thermophoretic losses can be somewhat reduced via reduction of the thermal gradient between the wall and the bulk gas. The use of high temperature sampling lines is unlikely to be problematic with ammonia, as spontaneous dissociation is thermodynamically unfavourable at temperatures < 200°C (approximately), while the temperatures commonly used in heated sampling lines used in automotive emissions analysis for compounds such as ammonia typically do not exceed ~195°C. It has been reported that NH_3 sample losses attributable to wall adsorption are lower where the wall temperature is 191°C than where it is 113°C [37].

Figure 23 shows an example of a lack of agreement between instantaneous NH_3 emissions rates from a simultaneous measurement performed using two different NH_3 analysers. The differences result from differences in the measured NH_3 concentrations, with a clear tendency for the Fourier Transform Infra-Red (FTIR) analyser to report lower peak concentrations and show longer response times than the Tuneable Diode Laser (TLD) analyser.

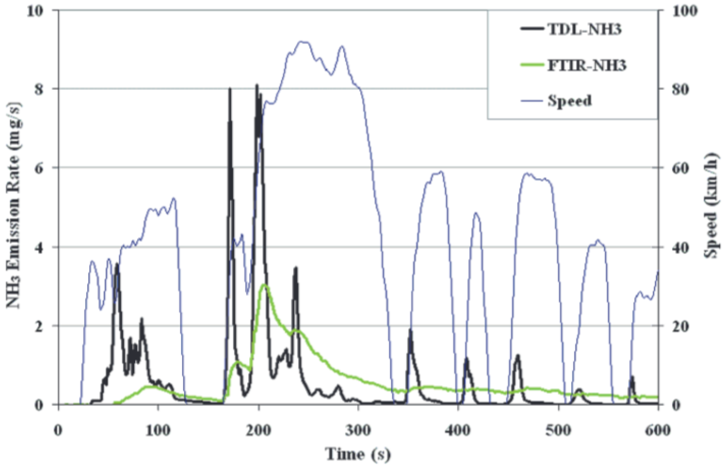

Figure 23. Real-time NH_3 emissions rate for a single test on a single vehicle, using two separate analysers with differing detection principles. Image source: [310]

A further example from measurements carried out using three different analysers measuring the emissions from 4 vehicles is shown in Figure 24.

There is widespread agreement in the literature that the CVS-bag method (using a constant volume sampler and conveying the sample to a bag for batch analysis after the sampling period has concluded) is not appropriate in the case of measurements of ammonia [115], [285], [311], [312]. Indeed, a literature review did not reveal a single study published within the last 20 years which employed *only* a dilute measurement technique; in all cases where diluted measurement approaches were confirmed, the authors noted significant memory effects, sample loss and generally unsatisfactory measurement parameters when analysing diluted exhaust gas. Indeed, two sperate studies employing such a technique [115], [312] noted long-lasting NH_3 memory effects, even enduring on the order of several hours. The primary reasons for this are: the high stickiness of ammonia (strong tendency to adhere to surfaces over which it flows) and the relatively large surface area of the dilution/sampling system, as well as the materials used in the exhaust gas transfer, dilution and sampling systems, which are not designed with quantification of unregulated emissions such as NH_3 in mind.

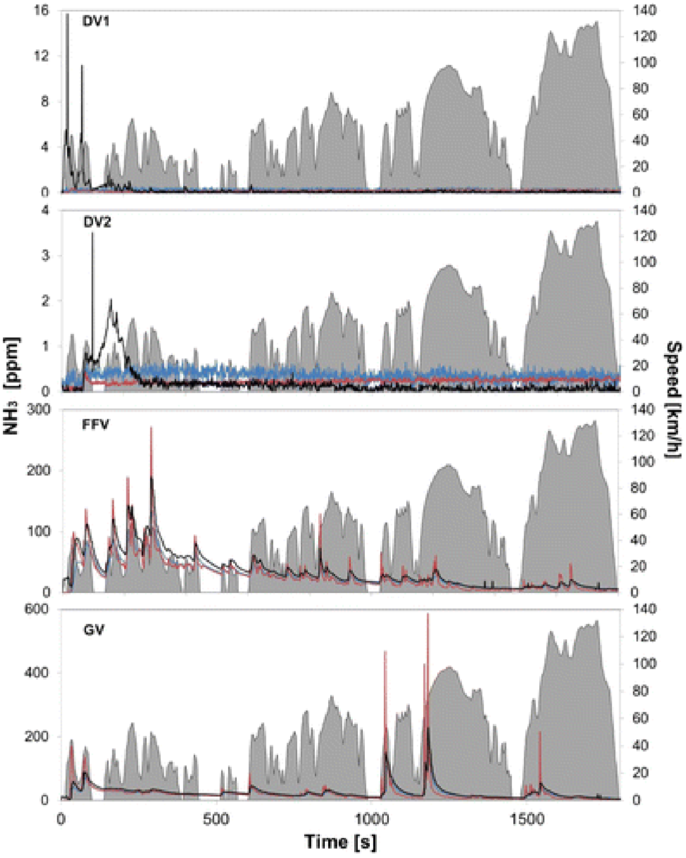

Figure 24. Real-time NH_3 concentrations from tests conducted on four vehicles, using three separate analysers with differing detection principles. Image source: [7]; refer to [7] for the legend of the vehicle types and analyser details (line colours)

The phenomenon of ammonia adsorption on the surfaces of solid materials (including various polymers and metals) is also of great relevance, since the vehicle's exhaust line is typically made of stainless steel. Thus, notwithstanding efforts to avoid the use of metal components in the sampling system leading to the NH_3 analyser, it is essentially inevitable that some of the NH_3 leaving the TWC will adsorb onto the metal over which it passes on its journey to the tailpipe. However, such effects are not restricted to the laboratory and will also occur when vehicles are used on public roads. If during a period of ICE operation a TWC begins to produce ammonia and the majority of that NH_3 adsorbs to the metal surfaces in the exhaust line, it is possible that the capacity of the exhaust line will be sufficient such that the journey ends before significant quantities of NH_3 are released from the tailpipe. In such cases, the question arises as to the long-term fate of adsorbed NH_3.

Hoard et al. [37] note significant NH_3 storage on the samples lines used to convey the exhaust gas sample from an automotive aftertreatment system to an NH_3 analyser, within the context of choosing materials for sampling lines for measurements of NH_3 in the aforementioned experimental setup. One of the considered materials in [37] was stainless steel, which can be considered a good proxy for the materials used in the exhaust line as well as sample transfer systems in many automotive emissions testing systems.

Spontaneous adsorption of a gas onto a solid results in a decrease in entropy and thus is an exothermic process, meaning that desorption is endothermic [313]. For that reason, an increase in the temperature of the system ought to reduce the thermodynamic favourability of adsorption and increase the favourability of desorption – and thereby shift the equilibrium towards release. This thus supports the hypothesis encountered in the literature that increasing system temperatures are increasingly unfavourable for further adsorption and should eventually cause release, as well as the general observation that storage and release effects in automotive emissions measurements are most severe following cold start. However, it is worth recalling that the exhaust system of an engine used in LD road transport rarely experiences an increase of temperature in isolation – such a change is typically accompanied by other changes, such as a dramatic increase in the flow rate of the exhaust gas (with attendant changes such as space velocity).

While an SI engine is running, there is a very high concentration of water vapour (~13% vol.) present in the exhaust gas. The ambient temperature, the temperature of the exhaust line and the geometry of the exhaust system also have varying impacts on the longevity and form of water in the exhaust system after the ICE has ceased to run (i.e. following shutdown). Gradual desorption of NH_3 may occur under such conditions, since no further NH_3 is being produced and free gaseous NH_3 present in the exhaust line should be expected to gradually diffuse out of the exhaust system; the equilibrium should shift in favour of desorption. Here a difference between legislative testing and real-world scenarios presents itself – the vast majority of emissions tests cycles used for vehicle testing end with an extended deceleration event, followed by a short period of idling. For example, the current EU legislative test cycle WLTC ends with a deceleration event lasting 70 seconds, followed by 6 seconds' idling. Thus, the final portion of the test is generally associated with very low NH_3 production, but should facilitate significant desorption of NH_3 (if present); indeed NH_3 concentration traces sometimes show a brief surge of this type which can, in most cases, be attributed to outgassing from metal surfaces.

The capacity of any metal to adsorb NH_3 onto its surface is finite and the process is reversable [37], [314]; the limiting value (number of molecules per unit surface area) is determined by gas stream characteristics (NH_3 concentration, pressure, temperature, competition effects from other species, including water) and the temperature of the substrate. Thus, if the surface of a given metal is exposed to a NH_3-contaning gas stream, after some period of time the surface will become saturated and no further NH_3 will be adsorbed, at least at a given temperature [37]. As stainless steel is used not only as the primary material for exhaust lines, but also as an important material for sampling exhaust gas for chemical analysis, the question of the degree of interaction and tendency for storage and release effects of NH_3 with stainless steel is therefore of great importance to the subject considered here. Some other materials are commonly used in analysers designed for the measurement of NH_3 concentrations and the sampling lines (for example, PTFE, as considered in [37], [308]). Specially developed coatings can be applied to stainless steel to minimise NH_3 absorption [306]. In addition to sample transfer, a further consideration regarding storage and release (and even apparent sample loss) concerns sample filtration. In automotive contexts, since the sampled gas stream is exhaust gas in its natural state, it contains non-gaseous pollutants in the form of particulate matter, which in the mid- to long-term can severely contaminate the analyser's tubing and even degrade the analyser itself, reducing its sensitivity and even rending it totally inoperable. Thus, a filter of some kind is commonly used, either of the disposable type, or a filter which can be removed, cleansed/regenerated and reinserted. In both cases, the potential for NH_3 sample loss via entrapment on the filter or via undergoing reactions with exhaust gas components adsorbed onto the filter (or even reactions with the filter itself) is clear; furthermore, since such filters usually have significant surface area and (unless in pristine condition) are also normally covered in a thin layer of highly porous ICE-derived particulate, the potential for short-term storage and release effects occurring on the filter itself should not be overlooked. Quartz glass-fibre filters have been shown to reduce the magnitude of these effects [7] and, through their widespread use, have been shown to provide acceptable durability in the high-temperature, particulate-laden corrosive exhaust gas environment.

5. Experimental work

5.1. Means employed to address the research tasks

5.1.1. Research method characteristics and justification of research strategy

A series of tests was conducted on a pool of vehicles (passenger cars) and on a single engine. A pool of passenger cars, being mainly of recent model year at the time of writing, were tested under laboratory conditions in a dedicated emissions laboratory using a chassis dynamometer (details follow).

HD vehicles with SI engines run either on petrol or, more commonly in markets with high fuel prices (such as the EU) on alternative fuels (mainly CNG/LNG). While in recent decades the overall share of SI ICE used in powertrains for the European HD sector has been low, certain vehicles types (e.g. buses) have a greater share of new CNG- fuelled powertrains than petrol SI powertrains [315]. Generally speaking, in-use HD SI powertrains remain dominated by units running on petrol [315], but in recent years the share of new HD vehicles running on alternative fuels has overtaken that of petrol, such that roughly 17 times as many newly registered HD SI powertrains run on alternative fuels (chiefly CNG/LNG) as on petrol [316]. Thus, it was decided to focus on a CNG HD engine;[11] experiments were conducted to characterise NH_3 emissions from such a powertrain. The engine was tested under laboratory conditions on an engine dynamometer (details follow). In all cases, commercially available analysers were used to measure concentrations of NH_3, in line with legislative requirements (where they exist), as well as common industry practice and good engineering judgement, the latter based in part on experience from the involvement of the author in similar testing of previous type.

5.1.2. Research objects

Vehicles used for testing

A total of 50 vehicles were tested under laboratory conditions, using a chassis dynamometer. All vehicles were market-available European passenger cars with nominally stoichiometric SI engines approved to the Euro 5 or Euro 6 standards and with mileages ranging from ~200 km to ~120,000 km (and thus ~0.1% to ~75% of assumed full useful life according to Euro 5/6 legislation). Some 60% of the 50 vehicles featured idle stop systems (also known by the names Stop & Start and other similar nomenclature); one vehicle was a mild hybrid and two vehicles were full hybrids, of which one was externally chargeable (so-called plug-in hybrid).

Detailed data of the test vehicles are given in Table 4.

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[11] In terms of emissions phenomena, it is well known that there are no significant differences between CNG and LNG engines; the form in which the fuel is stored before delivery to the cylinder has not been shown to have any detectable impact on the combustion, pollutant formation or exhaust aftertreatment processes.

Table 4. Test vehicle data

Vehicle ID	Hybrid powertrain details (if any)	Approx. combustion engine displacement [dm^3]	Fuel type, fuel delivery system	Approx. engine power [kW]	Charging system	Aftertreatment system type	Emissions standard	Applicable EU type approval procedure	Approx. mileage(s) during testing [km]
1	None	1.5-2.0	Direct injection	110-130	Turbocharged	Close-coupled TWC (1)	Euro 5	NEDC	60000
2	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	20000
3	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	1000
4	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	15000
5	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	10000
6	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	2000
7	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	20000
8	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	60000
9	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 5	NEDC	3000
10	None	1.0-1.5	Indirect injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	85000
11	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	40000
12	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	50000

13	None	1.5-2.0	Direct injection	110-130	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	20000
14	None	1.5-2.0	Direct injection	110-130	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	60000
15	None	1.5-2.0	Direct injection	110-130	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	60000
16	None	1.0-1.5	Indirect injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	20000
17	None	1.0-1.5	Indirect injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	20000
18	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	85000
19	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	85000
20	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	NEDC	85000
21	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	200
22	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	200
23	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	10000
24	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	10000

25	None	1.0-1.5	Indirect injection	50-70	Naturally aspirated	Close-coupled TWC (1)	Euro 6	NEDC	85000
26	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	WLTP	500
27	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	WLTP	15000
28	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)	Euro 6	WLTP	25000
29	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	40000
30	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	40000
31	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	60000
32	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	60000

33	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	40000
34	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	80000
35	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	80000
36	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	80000
37	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	100000
38	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	100000
39	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	120000

40	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	60000
41	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	60000
42	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	70-90	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	60000
43	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	90-110	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	60000
44	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	90-110	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	20000
45	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	90-110	Turbocharged	Close-coupled TWC (1)+GPF	Euro 6	WLTP	120000
46	Micro hybrid (idle stop system)	1.0-1.5	Direct injection	100-120	Turbocharged	Close-coupled TWC+GPF (1)	Euro 6	WLTP	10000
47	None	5.0-6.0	Indirect injection	280-300	Naturally aspirated	Close-coupled TWCs – one	Euro 6	WLTP	1000

						per cylinder bank (2)			
48	Mild hybrid (series)	3.0	Direct injection	310-330	Turbocharged	Close-coupled TWCs – one per cylinder bank; underfloor TWCs+GPFs – one per cylinder bank (2; 2)		WLTP	20000
49	Full hybrid (NOVC)	1.5-2.0	Indirect injection	80-100	Naturally aspirated	Close-coupled TWC (1)	Euro 6	WLTP	20000
50	Full, plug-in hybrid (OVC)	1.5-2.0	Indirect injection	80-100	Naturally aspirated	Close-coupled TWC (1)	Euro 6	WLTP	30000

Engine (powertrain) used for testing)

Experiments were carried out on a HD CNG engine, which was type approved as an HD unit. A single engine was tested, being a turbocharged CNG-powered monofuel engine of displacement ~3 dm^3 and rated power approximately 100 kW. The engine was nominally stoichiometric and was equipped with a two-part aftertreatment system, consisting of a close-coupled initial TWC and a second TWC of greater volume located some distance downstream of the initial TWC, as is commonly encountered for many HD CNG engines. The engine was installed on the engine dynamometer in precisely the configuration which would be used for type approval of such an powertrain, with exhaust emissions measured directly downstream of the final element of the aftertreatment system (i.e. the main TWC).

5.1.3.Test equipment employed

Overview of chassis dynamometer facilities for vehicle testing

All vehicle-level emissions testing was performed in a climate controlled chassis dyno exhaust emissions laboratory at BOSMAL Automotive Research and Development Institute Ltd (Bielsko-Biala, Poland). This vehicle emissions testing facility features a 48” single roller twin-axle drive chassis dynamometer and a range of equipment for quantification of regulated and unregulated exhaust emissions. The specification of the aforementioned equipment meets (or exceeds) the EU requirements for legislative exhaust emissions testing at the time of writing; the facility’s specification is also closely aligned with the applicable US, Chinese and Japanese requirements for testing of light-duty vehicles. Key details of the laboratory from the point of view of the testing described in this section are given below; a schematic overview is shown in Figure 25; note the presence of the quantum cascade laser (QCL) analyser and the fact that it is connected directly to the test vehicle’s tailpipe. See also [317] for further information on this test facility.

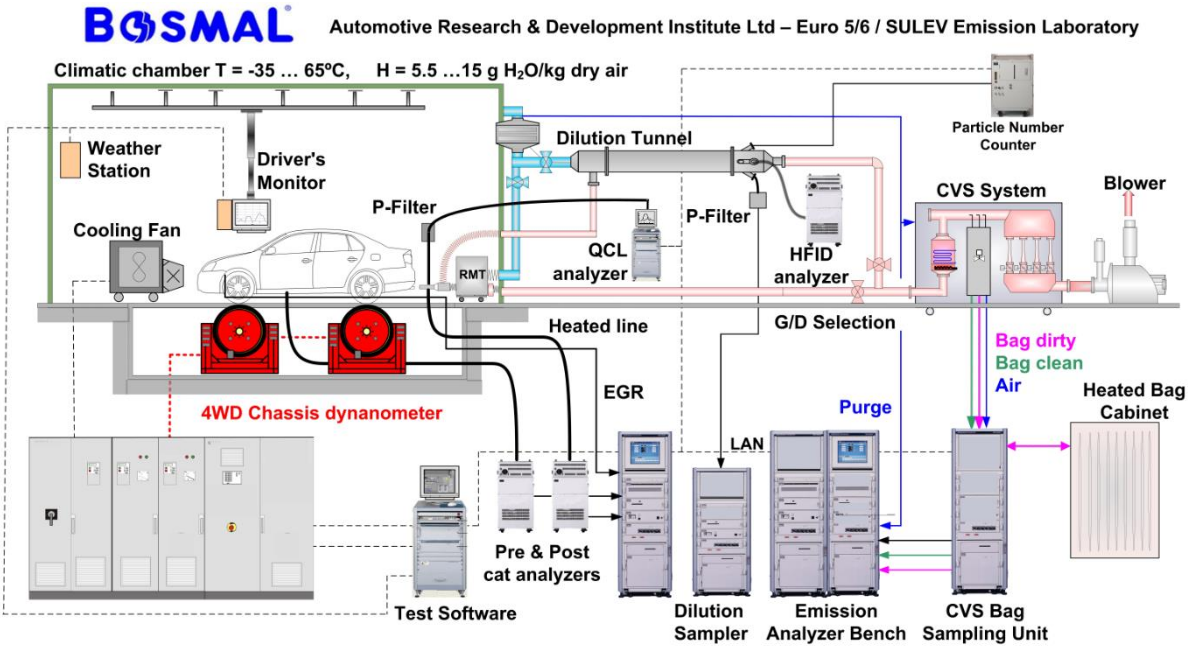

Figure 25. Schematic overview of Exhaust Emissions Laboratory No. 2 at BOSMAL

The chassis dynamometer (AVL, Austria, 2014) permits accurate recreation of idealised road load conditions for vehicles of inertia 454-5448 kg. The additional roller axle permits vehicles to be tested with all four wheels rotating, which increases the level of realism of the road load simulation and (in certain cases) permits vehicle systems such as idle stop systems to function as they would if the vehicle were physically in motion. The industry standard roller diameter of 48" (1219.2 mm) is widely considered sufficient to closely approximate the traction of a wheel of the size used in LD vehicles over a flat surface and does not require that tyres be overinflated for testing. The maximum supported speed is 250 km/h and when used in twin axle mode the speed synchronisation between the rollers meets the EU and US requirements on that point. The tolerance of the controlled tractive force is ±0.2% of the full scale; the tolerance of the speed measurement is ±0.02 km/h. A vehicle fixation system based on rigid bars and floor anchors of adjustable height allows the vehicle under test to be secured in a safe manner, limiting lateral and longitudinal motion as low as reasonably practicable. Some vertical motion must be permitted, as reflected in the design of the restraining system, yet the mounting system minimises the chances of wheel slip, even during demanding driving cycles featuring high rates of acceleration occurring from a standing start. In most cases, the force coefficients used for road load simulation were obtained by means of road load matching (the well-known so-called coast down method), in line with industry norms, as well as EU legislation (and broadly in line with US requirements). Where target road load data were lacking, either road load data were calculated based on the generic equations provided in EU legislation, based on vehicle mass and frontal area, or the alterative final dynamometer loading models from UNECE Regulation No. 83 were used (based on vehicle mass alone). Note that all three of the aforementioned approaches to road load simulation are in common use in the European automotive industry and all have precedents in EU automotive emissions legislation. It is, however, important to note that in the majority of the chassis dyno testing reported in this work the applied road load was not identical to that applied during type approval.

While regulated exhaust emissions (as defined in the Euro 6 standard) are not the primary focus of this thesis, their quantification during tests focusing on RNC emissions is warranted, from several points of view: to provide results relating to regulated emissions and fuel consumption to allow for plausibility parsing of test results; to provide comparison bases for emissions measurements performed using alternative quantification methods. For those reasons, regulated emissions were measured according to the EU legislative test method, during all emissions tests. The emissions laboratory features analysers produced by Horiba (2008) specifically designed for quantification of regulated emissions via the legislative CVS-bag method[12].

The laboratory also features analysers of broadly similar type, sampling a continuous undiluted stream of exhaust gas, labelled "Pre & Post cat analysers" in Figure 1. The compounds quantified by those analysers are: THC, CH_4, NMHC*, CO, CO_2, NO, NO_2*, NO_x; the species marked with an asterisk are calculated on the basis of other results, namely: THC – CH_4 = NMHC; NO_x – NO = NO_2. Self-evidently, the concentration of pollutants (and water) in undiluted exhaust gas samples greatly exceeds that of the diluted exhaust gas sample; for that reason, the pre and post cat lines feature higher ranges of measurement and high-temperature sample pre-treatment (191°C). These analysers are not required for legislative emissions measurements and their design and functionality is guided by industry requirements and unwritten consensus regarding best practice. Measurements of undiluted exhaust gas performed with analysers of this type were included in some cases (but not in all emissions tests).

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[12] As defined in EU legislation. Note however, that the specific technical requirements of this approach are very similar to those required for automotive certification testing in all automotive markets with advanced emissions requirements (including, the USA, Japan, China, etc).

A dedicated automotive RNC analyser was used to quantify concentrations of RNCs in undiluted exhaust, with a focus on NH_3. The RNC analyser was produced by Horiba (Japan, 2017) was of quantum cascade laser (QCL) type. This device provides simultaneous measurements of the concentrations of NO, NO_2, N_2O and NH_3 in undiluted exhaust gas and is specifically designed for such measurements. The unit's key characteristics are shown in Table 5.

Table 5. Characteristics of the RNC analyser used in the experimental work performed at the vehicle level (chassis dynamometer testing)

Aspect	Details
Detection principle	Quantum cascade laser infra-red (QCL-IR) spectroscopy
Sample pre-treatment	Heated transfer line (113°C), heated prefilter with exchangeable quartz-based cartridge
Sample flow rate	8 dm^3/min ±1 dm^3/min
Measurement frequency	10 Hz; data archival at either 1 Hz or 10 Hz
NH_3 ranges	(Low) 0 ppm to 5 ppm/50 ppm, (High) 0 ppm to 200 ppm/ 2000 ppm
NO ranges	(Low) 0 ppm to 10 ppm/100 ppm; (High) 0 ppm to 500 ppm/ 5000 ppm
NO_2 ranges	(Low) 0 ppm to 5 ppm/50 ppm; (High) 0 ppm to 200 ppm/ 2000 ppm
N_2O ranges	(Low) 0 ppm to 10 ppm/100 ppm, (High) 0 ppm to 500 ppm/ 2000 ppm
Stated NH_3 T_{10}–T_{90} response time	within 2.5 s
Stated NO T_{10}–T_{90} response time	within 1.5 s
Stated NO_2 T_{10}–T_{90} response time	within 1.5 s
Stated N_2O T_{10}–T_{90} response time	within 1.5 s

Certified calibration gases for each of the ranges for each of the RNCs were used for calibration (span correction) purposes. The span gas concentration values were within the range 70-85% of the full scale concentration.

While instruments of this type are not directly subject to legal requirements for LD vehicle testing, it is worth noting that the QCL analyser employed here fulfils the demands of the additional pollutants section of GTR No. 15 (WLTP test method), as well as EU HD legislation for engine dynamometer type approval testing. The QCL analyser was subject to annual overhaul and maintenance procedures, performed by the manufacturer.

The QCL analyser was calibrated before each use in accordance with the manufacturer's instructions and was thoroughly purged with ambient air before and after each emissions test. The filter was changed after every 5 hours of measurement (i.e. emissions testing) had elapsed.

In the course of the experimental work, the following quality control measures were implemented:

- Validation of NO_x emissions measured via QCL against the NO_x emissions measured by the legislative bag method (chemiluminescent detector, CLD). The pass/fail criterion used was ±5%. In cases where NO_x emissions were very low (< 12 mg/km, i.e. < 20% of the applicable Euro 5/6 limit), this criterion was extended to ±15%, but for the most part the 5% criterion was met by the results obtained.

- Regular plausibility and NH_3 hang up checks achieved by measuring using the QCL analyser without a vehicle connected to the exhaust gas transfer system. In cases where the measured 30-second mean NH_3 concentration was not within the range 0–1.0 ppm[13], the exhaust transfer system was purged with ambient air at a flowrate of approximately 200 dm^3/s for at least 300 seconds, and then the check was repeated. During the aforementioned period of purging of the exhaust transfer system, the QCL analyser itself was purged with ambient air.
- An initial correlation activity was performed, consisting of validation of NH_3 concentrations achieved via measuring with a second, entirely separate NH_3 analyser meaning in parallel. The second NH_3 analyser (AVL, 2017) featured a different detector type (laser diode detector, LDD), but also fulfilled all applicable requirements (GTR15 Additional pollutant; EU HD engine type approval requirements). A total 5 of emissions tests performed on vehicles similar to those characterised in this experimental work revealed close agreement of both instantaneous and mean NH_3 concentrations, with R^2 values for time-shifted instantaneous concentrations of falling within the range 0.89–0.96 and mean concentrations typically agreeing to within 5–10%.

Vehicle road load was set by matching the road load data declared by the vehicle manufacturer; where unavailable, the alternative procedure provided for in EU legislation were employed. Vehicles were preconditioned by driving the driving cycle to be used in the emissions test between 10 and 24 hours before the emissions test itself took place and in the interim the vehicle was heat soaked at a nominal temperature of 23°C. For the NEDC, gearshifts as proscribed in the legislation were used; for WLTC testing the legislative method to determine gear shifting was employed; for all other tests gears were changed according to the recommendations of the gear-shift indicator – if not present, then gears were changed at the driver's discretion. All vehicles featuring automatic gearboxes were tested in automatic mode. Charging of vehicle batteries was only carried out before NEDC tests; for all other tests the state of the battery was "as found" following the previous period of engine operation[14]. All cabin accessories (including air conditioning) were turned off. For cycles commencing from cold start, this condition was considered to be fulfilled if the following two conditions were both satisfied at the time of test start:

- $\geq$ 8 hours elapsed since last period of powertrain operation,
- temperature of engine coolant within 2°C of ambient temperature; i.e. for tests conducted at 23°C, coolant temperature $\leq$ 25°C in all cases.

For the test cycles commencing from hot start, this condition was considered to be fulfilled if the following three conditions were all satisfied, simultaneously, at the time of test start:

- $\leq$ 15 minutes elapsed since last period of powertrain operation (note that for hybrid vehicles powertrain operation is not necessarily synonymous with engine operation),
- engine coolant temperature > 70°C.

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[13] The noise value for NH_3 (lowest range) given by the QCL manufacturer is 0.2 ppm or less. In practice, with the sampling system connected to the exhaust gas transfer tube, the NH_3 concentration noise level was frequently found to exceed this value; extended purging with ambient air of relative humidity ~50% did not decrease the value below 0.2 ppm. For the quality control purposes mentioned above, the acceptable noise limit was thus increased to 1 ppm, mindful of the fact that this equates to 10% of the reference level (the EU HD mean concentration limit of 10 ppm).

[14] This point is of relevance to the topic at hand, since the battery's state of charge upon engine startup has, in most cases, an appreciable and entirely quantifiable influence on fuel consumption via the load exerted on the engine by the alternator.

Overview of engine dynamometer facilities for powertrain testing

Engine test cell number 14 at BOSMAL Automotive Research and Development Institute Ltd (Bielsko-Biala, Poland) was used for this testing. This test facility features an automated engine dynamometer control system (AVL PUMA, AVL iGEM), with analysers for regulated emissions meeting the applicable EU standards (at the Euro VI level), capable of meeting all the requirements imposed by the relevant Euro VI HD legislation [318]. The engine dynamometer operates within the speed range 0–7500 rpm and in the torque range 0–750 Nm; the accuracies for those parameters are ±1.25 rpm and ±1.5 Nm, respectively. The test cell's fuel supply system provides fuel (in this case CNG) to the engine. Ammonia was quantified via a dedicated automotive NH3 analyser (AVL LDD, 2013) which met all relevant demands relating to HD NH3 measurement [318] and had a full range of 0-1500 ppm, a nominal accuracy of ±2% of the measured concentration and a sample flow rate of 8 dm^3/min. (Note that this analyser was the same unit that was used for the aforementioned correlational analysis with the QCL analyser used for chassis dynamometer testing.) In the case of powertrain testing, time alignment of concentration signals is considered to be of lower importance, due to the fact that the sampling point is very close to the outlet of the final element in the aftertreatment system. For this reason, a single time correction value was applied to the NH3 concentration measured in the engine dynamometer laboratory. The NH_3 analyser's filter was changed after every 4–5 hours of powertrain operation. Testing was performed using the transient (non-steady state) test procedure mandated for engine type approved according to Euro VI requirements, namely the World Harmonised Transient Cycle (WHTC) [319], which is run from both cold start and hot start, with results from the two procedures (cold/hot) subject to final weightings of 0.14 and 0.86, respectively.

Conversion of exhaust gas concentrations into gravimetric emissions factors

The analysers used in the chassis dynamometer and engine dynamometer laboratories, as specified in the previous sections, report a concentration signal in ppm. Mathematic processing of this concentration vector is briefly described here.

For vehicle testing performed in the chassis dynamometer environment, concentrations measured in the raw, undiluted exhaust gas (regardless of analyser type) were converted into gravimetric emissions by multiplying the flow rate calculated on the basis of the dilution factor (i.e. the so-called CO_2 tracer method), with time alignment of the CO_2 concentration vector performed in accordance with sound engineering practice. In practical terms this meant aligning the CO_2 with the speed trace, particularly focusing on periods of acceleration, but also partly based on the calculated linear gas velocity based on the CVS flow rate. Note that this approach is a quasi-standardised method widely used in the automotive industry; it is, however, not part of the certification procedure and is not subject to any legislative precedent. For engine-dynamometer based powertrain testing, the legislative test method only requires measurement of concentration, with no conversion to gravimetric emissions required by the legislation. However, the legislative method from conversion of concentrations to gravimetric results was applied, in order to obtain work-specific gravimetric NH_3 emissions results.

5.2. Results and discussion

5.2.1. Comparison of the mean concentrations of NH_3 in vehicle exhaust to the available legal precedent, i.e. the EU HD NH_3 concentration limit

Test results from all 51 vehicles were analysed in order to assess compliance with this emissions control precedent – i.e. 10 ppm mean concentration limit. The testing approach adopted in this stage of the investigations was to apply the test procedure used for type approval of the vehicle in question (i.e., NEDC or WLTP; refer to Table 1). The entire set of mean concentration results obtained from all vehicles are shown in Figure 26 in the form of a box-and-whisker diagram[15].

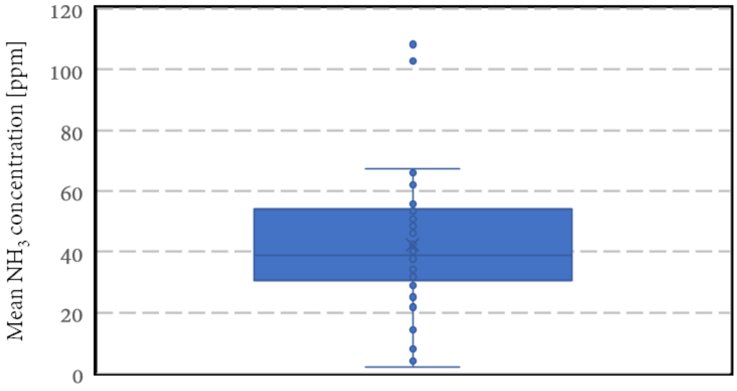

Figure 26. Box-and whisker diagram showing mean NH_3 concentration results from all 50 vehicles tested

Note that in Figure 26, all vehicles are treated as a single population, i.e. the boxplot has only one category and the width of the rectangle representing the interquartile range is arbitrary. Note also that the figure shows results obtained using two different test procedures (NEDC and WLTP). Datapoints are shown, due to the existence of outlying results exceeding the upper whisker bar range; note the substantial margin by which the outlying results exceed the upper whisker. The relatively low number of visible datapoints results from very dense overlapping of datapoints within the interquartile range.

The overall, unequivocal finding was that the EU HD limit chosen used as the only legally-valid reference level (10 ppm) was exceeded in the vast majority of cases – often by a large margin; note the magnitude of the lower boundary of the interquartile range (some 31 ppm, i.e. just over 3 times the aforementioned reference level). The two highest emitters had mean NH_3 concentrations >100 ppm, i.e. >1 order of magnitude above the reference level; however, the plot shows these points to be unequivocal statistical outliers, since they lie far outside the upper whisker. The results from the lowest emitting vehicles lay much closer to the normal distribution; a total of 4 vehicles (i.e. 7.8% of the population) showed mean NH_3 concentrations < 10 ppm, which would have thus met EU HD requirements on that point. All of these four low emitting vehicles shared certain characteristics, namely hybridisation, high engine power/displacement, or both. These vehicles were:

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[15] Proposed by the statistician Tukey in 1977, box-and-whisker plots (also known as box-plots or boxplots) are a means of conveying statistical information in a concise visual format. They show a concise graphical summary of 6 key quantitative data metrics: "minimum", first quartile (Q1), median, mean, third quartile (Q3), and "maximum". The box's upper and lower boundaries are Q1 and Q3, i.e the box represents the interquartile range. The whiskers, representing minimum and maximum, are determined by extending the interquartile range by 50%. Box-and-whisker plots with datapoints allow data points lying above the "maximum" whisker or below the "minimum" whisker to be identified as outliers.

- two of the full hybrid vehicles – vehicles 49 and 50
- vehicle 48, a mild hybrid vehicle featuring an engine of large displacement and a high vehicle power:weight ratio vehicle
- vehicle 47, which featured a fully conventional ICE (i.e. no hybridization whatsoever) but with technical characteristics of which make it an outlier in terms of the overall characteristics of the EU passenger car fleet.

As the histogram below (Figure 27) shows, the majority of observations lay within the range 10–59.1 ppm, i.e. between 1 and ~6 times the aforementioned reference level of 10 ppm. A total of 10 observations exceeded 59.1 ppm, thus outnumbering by more than 3:1 the number of observations below 10 ppm, which numbered only 3.

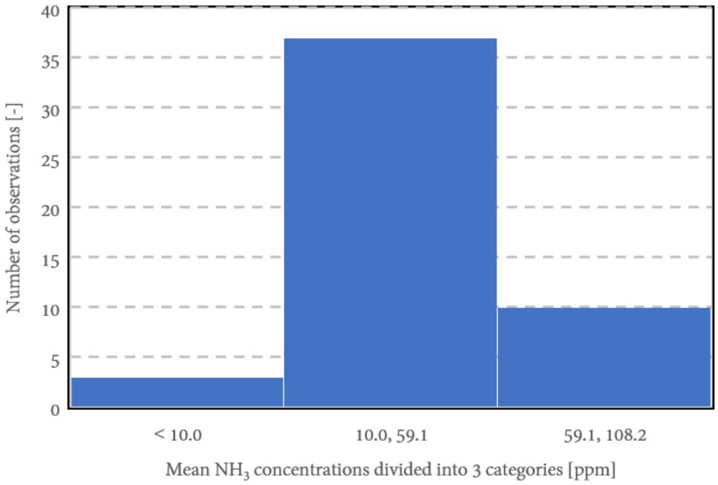

Figure 27. Histogram showing mean NH_3 concentration results from all 50 vehicles tested, with the first category representing the reference concentration (see the text for discussion)

Dividing the same data into 5 categories of equal width, a heavily skewed, non-normal distribution becomes apparent, as shown in Figure 28.

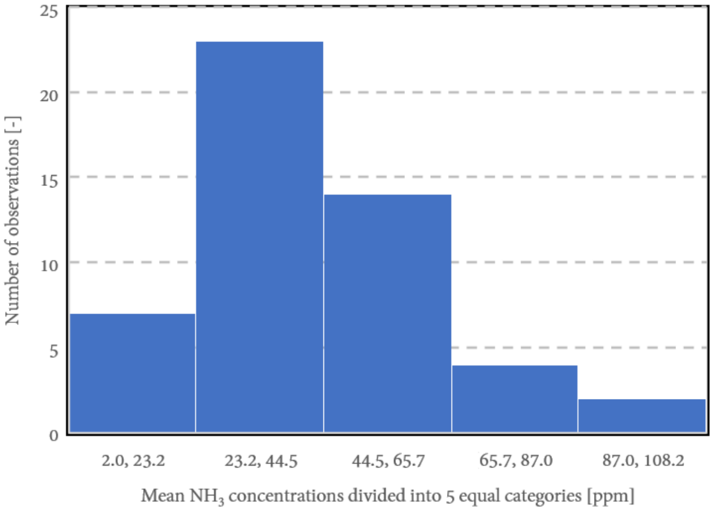

Figure 28. Histogram showing mean NH_3 concentration results from all 50 vehicles tested, divided into 5 equal categories

While the aforementioned reference point based on legal precedent is concentration-based, the normal approach used in LD emissions control, which is strongly expected to also be adopted in the case of NH_3 for the forthcoming Euro 7 standard, is to use distance-specific gravimetric emissions. The gravimetric NH_3 emissions from the same dataset are shown in Figure 29.

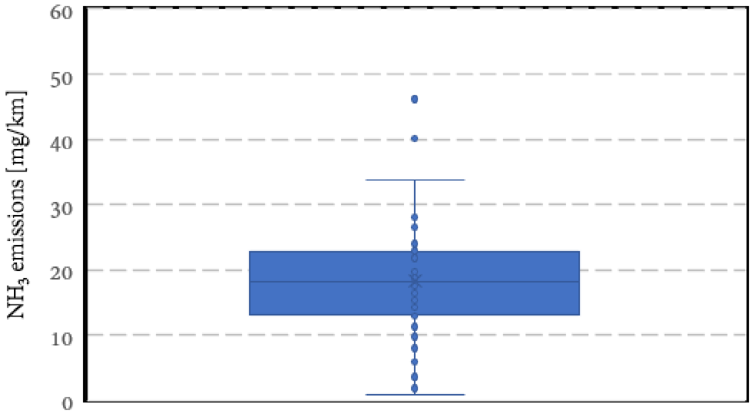

Figure 29. Box-and whisker diagram (with datapoints) showing distance-specific gravimetric NH_3 emissions results from all 50 vehicles tested

As suggested by the wide range of mean concentration values (see Figures 26–27), the gravimetric emissions of the 50 vehicles also covered a wide range, amounting to approximately an order of magnitude. The upper value of the interquartile range was just under 24 mg/km – this finding is significant, as it is very close to the reference level (the Euro 5/6 NO_x limit of 60 $mgNO_x$/km equates to 22.2 $mgNH_3$/km, on a molar basis)[16]. The values covered by the interquartile range were for the most part somewhat higher than values recently reported for Euro 6d-TEMP and Euro 6d vehicles [131]. However, the highest NH_3 emissions reported in [136] for the WLTC cycle were close to the highest values shown in Figure 5. The mean and median values shown in Figure 5 were almost identical at 18.3 mg/km, i.e. some 75% of the aforementioned reference level. NO values lay below the lower whisker; 10 vehicles showed emissions < 10 km/km. It should be noted that that the appliable Euro 5/6 NO_x limits were met during all test results included here, in most cases by a considerable margin (80% of the vehicles emitted < 35 $mgNO_x$/km, i.e. <58% of the limit). In this context, it should be recalled that the Euro 5 and 6 limits applicable to gaseous emissions from SI engines are identical for both emissions standards and that the emissions durability requirement (160,000 km) is the same for both emissions standards. Significantly, the range of gravimetric NH_3 values found for the entire pool (vehicles 1–50; Figure 5) and the subset has very little overlap with the data presented in a compendium of NH_3 emissions factors complied in 2009 considering studies from 1993-2006 [119], for which the mean value was approximately 41 mg/km.

As the ratio of NH_3 to other RNCs in the exhaust is of relevance to such discussions, the molar NH_3 RNC fraction $\{NH_3\}$ derived from the same dataset is shown in Figure 30.

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[16] When converted on a molar basis and assuming that all NO_x occurs as NO_2 (as has been assumed in all Euro standards to date, including Euro 6).

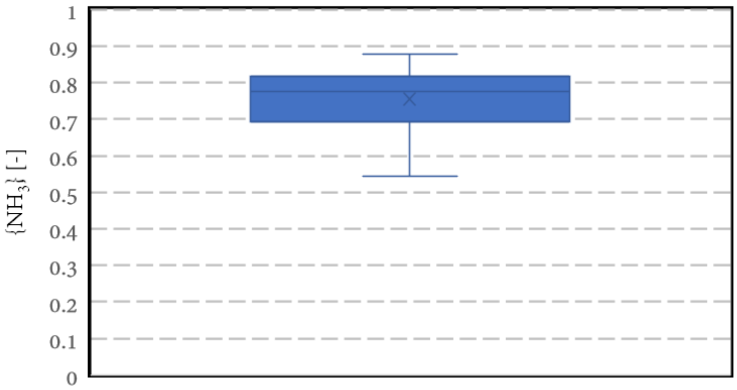

Figure 30. Box-and-whisker plot of {NH_3} values obtained over the WLTC or NEDC (as applicable) from vehicles 1-50

The mean and median both took values of approximately 0.75 and the interquartile range is bounded by the values 0.69 and 0.82. The upper whisker reaches a value of 0.88 and the lower whisker takes a value of 0.54, thus strongly supporting the assertion – oft-encountered in the literature – that NH_3 is the dominant RNC species in the exhaust gas for SI vehicles with low NO_x emissions (i.e. those with well-functioning TWCs); see [320] and [321], and references therein, as well as [146]. Focusing on the range of values of {NH_3} which can be interpreted as representing the majority of datapoints (i.e. the interquartile range), the values shown are markedly higher than some previously reported values (e.g. [132]) and represent the very upper end of the 0.4-0.8 range mentioned by Heeb at al. [118]. When comparing this finding with that reported by Heeb et al. well over a decade ago, the increased stringency of the applicable NO_x limit may be a significant factor, as well as the dynamic and relatively demanding speed trace of the WLTC, which features frequent accelerations and essentially no periods of constant speed (apart from stationary idling).

5.2.2. Characterisation of NH_3 emissions from vehicles representative of the latest powertrain trends for non-hybrid vehicles

Due to the wide range of emissions results presented in the previous section, and the fact that the pool of 50 vehicles included both Euro 5 and Euro 6 vehicles, as well as two vehicles with engines of displacement ≥ 3 dm^3, it was decided to focus further on a sub-set of vehicles representing the most recent market-available powertrain trends for passenger cars in the EU. That is to say, vehicles with downsized, turbocharged engines which met the Euro 6 emissions standard and which had thus been type approved using the WLTP were chosen for further testing and analysis. Note that hybrids are dealt with in other sections and that the vehicles examined here were microhybrids (equipped with idle stop systems).

These vehicles (vehicles 26–46; n = 20) were all type approved to the WLTP and had mileages within the range 20000–120000 km. The statistical distribution of mean concentration results obtained during the applicable type approval test procedure (WLTP) showed a narrower range, with no outliers, as shown in Figure 31.

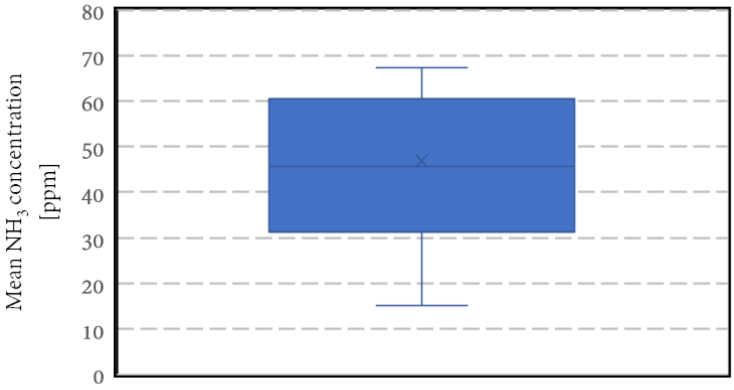

Figure 31. Box-and-whisker plot of mean NH_3 concentrations obtained over the WLTC from vehicles 26–46

Figure 31 does not show datapoints, due to the lack of outlying results. As the figure clearly shows, despite a lack of results > 68 ppm and with the upper quartile barely exceeding a value of 60 ppm, the plot confirms that mean concentrations significantly exceeded the reference level. In the case of this sub-set, the interquartile range spanned 30 ppm (31–61) ppm; the mean and median values were both approximately 45 ppm. The lowest measured value was 15 ppm – i.e. 50% higher than the reference level and significantly higher than the values from the aforementioned low emitting vehicles with mean concentrations < 10 ppm.

When converted to distance-specific gravimetric emissions, the same data show the distribution shown in Figure 32.

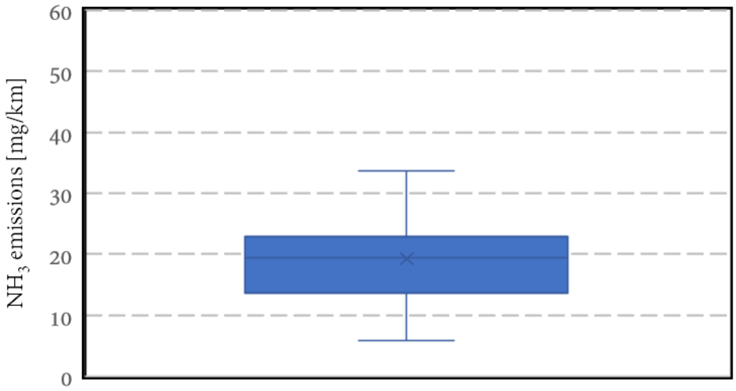

Figure 32. Box-and-whisker plot of gravimetric NH_3 emissions obtained over the WLTC from vehicles 26–46

Here the interquartile range is relatively small, spanning only some 10 mg/km and the mean and median values are essentially identical, lying at a value of 20 mg/km. It should be noted that these values are in fact slightly higher than the equivalent values for the entire pool (vehicles 1–50); the explanation offered for this is that the downsized engines were subject to relatively high specific load and that the lack of engines of high displacement and high engine specific power caused the mean and median NH_3 emissions to be higher than might be expected.

As mentioned in previous sections, while the WLTC is considerably more dynamic than the NEDC, with significantly higher energy demand per unit of cycle distance, the literature is not unanimous on which test cycle tends to produce greater NH_3 emissions[17]. In order to investigate this point for the vehicles of greatest interest, a subset of vehicles were also tested over the NEDC, in order to provide a direct comparison between the results obtained from the two test cycles. Results are shown in Figures 33 and 34.

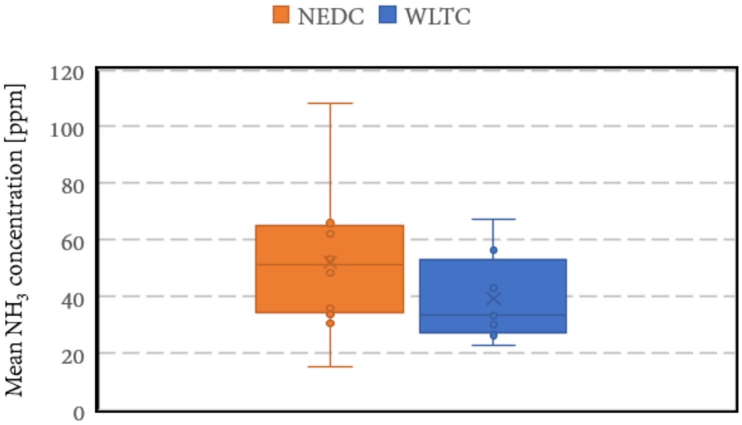

Figure 33. Mean NH_3 concentrations obtained over the NEDC and WLTC

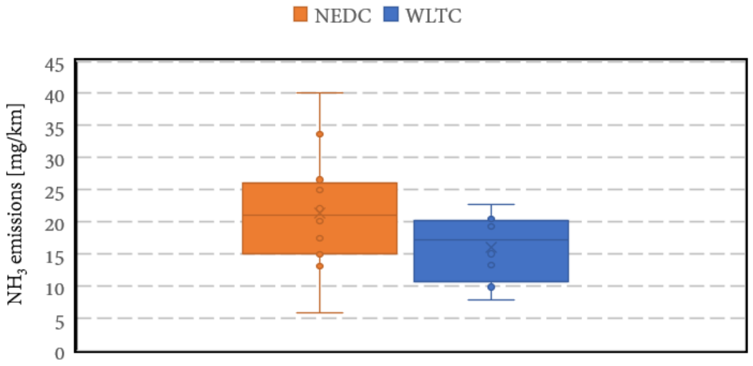

Figure 34. Gravimetric NH_3 emissions obtained over the NEDC and WLTC

It was hypothesized that the difference between the NH_3 emissions obtained over the two test cycles was primarily due to differences occurring during the first phase and the surge of NH_3 emissions that occurred therein. Examining the gravimetric emissions from the 1st phase of each cycle, it immediately becomes apparent that this was not the case and that the reverse was in fact true, as shown in Figure 35.

Results from WLTC Low are noticeably higher than those obtained over the UDC; the difference in the mean and median values is some ~9 mg/km and the interquartile ranges do not overlap, indicating a significant difference for the population as a whole. This might appear surprising, given the importance of NH_3 emissions from the cold start phase in determining emissions over the entire cycle. However, the distance covered during the cold start phase has an obvious impact on the distance-specific results. A simple calculation reveals that the difference in the distance covered during the initial phases of each cycle is far smaller than the total distance covered during the entire cycle – thus, results from the first

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[17] Recall that the speed trace is not the only relevant factor; road load simulation and the use of the gearbox (in the case of manual transmissions) are important determiners of engine rotational speed, load and thereby instantaneous fuel consumption and λ.

phase notwithstanding, the WLTC simply contains more warmed up operation with low-to-modest NH_3 emissions, meaning that despite the relative importance of the first phase, the tendency for the entire cycle is essentially inverted. The relative ratio values shown in Table 6 demonstrate the reasoning behind this assertion.

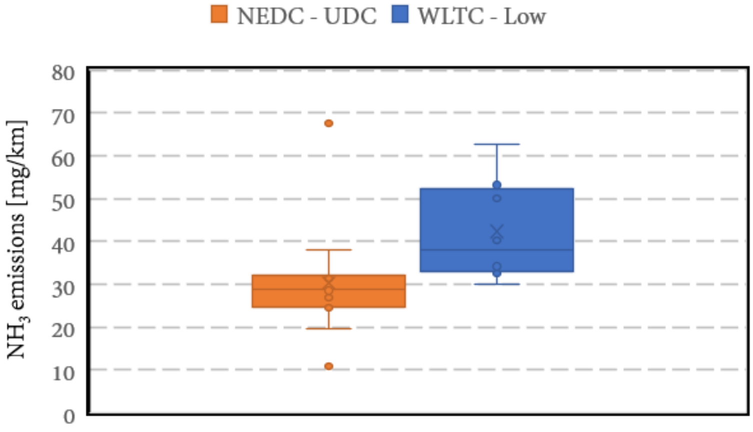

Figure 35. Gravimetric NH_3 emissions obtained over the initial (cold start) phases of the NEDC and WLTC

Table 6. Distances are derived ratios for NEDC and WLTC (entire cycle and their respective initial phases)

Phase/cycle	NEDC value [km]	WLTC value [km]	Ratio [-]
1st (NEDC-UDC; WLTC Low)	4.0	3.08	0.77
Entire (NEDC; WLTC)	11.0	23.3	2.12

5.2.3. Investigation into NH_3 emissions from low-emitting vehicles under more demanding driving conditions

Testing was performed to determine whether low emitting vehicles could be provoked into emitting higher levels of NH_3 emissions under certain conditions.

Two low emitters were identified, both of which had mean NH_3 concentrations <10 ppm when tested over the WLTC. As discussed below, the vehicles were not full hybrids (which are examined in another section). These vehicles had high power:mass ratios > 100 W/kg (compare the WLTP vehicle classification system, in which the highest category is for vehicles with values > 34 W/kg). One vehicle featured an engine of large capacity by EU market standards (~3 dm^3) and a mild hybrid system which provided additional torque during periods of high demand and was capable of providing exclusive power for vehicle propulsion at speeds to up approximately 5–6 km/h, which allows ICE startup to occur when the vehicle is already in motion. The other vehicle featured no powertrain hybridisation, but featured a combustion engine with 8 cylinders and a total displacement >5 dm^3. Both vehicles had low mileages (3000 km and 8000 km, respectively) and thus the long-term evolution of NH_3 emissions was not investigated for these vehicles. More demanding driving cycles were employed to determine whether the vehicles could be provoked into producing higher NH_3 emissions.

The vehicle with the mild hybrid powertrain was tested over several driving cycles other than the WLTC. The mean concentration remained < 10 ppm for all test cycles employed; the distance-specific gravimetric emissions are shown in Figure 36.

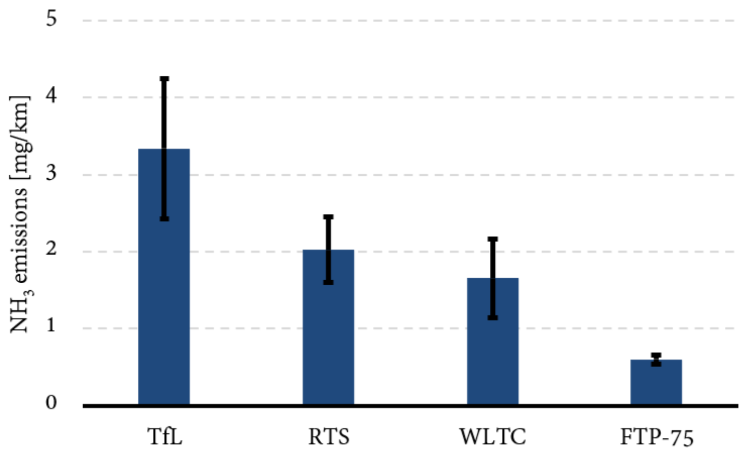

Figure 36. NH_3 emissions from vehicle 48 tested over 4 driving cycles with variable characteristics (all covering > 10 km and all commencing from a cold start)

As the plot shows, emissions over all cycles were very low, with no test result exceeding a value of 4.5 mg/km. The TfL cycle[18] showed the highest emissions, while the RTS[19] and WLTC were broadly equivalent and the FTP-75 showed by far the lowest emissions. As the TfL cycle, particularly its earlier stages, features a very low mean speed, with short sub-trips and frequent periods of standstill, this result is not unexpected, since the combustion engine frequently shut down and restarted. As Figure 37 shows, compared to the FTP-75, the total number of engine restarts is similar over the period 0–1200 seconds, but the number occurring by (say) 300 seconds shows a strong divergence.

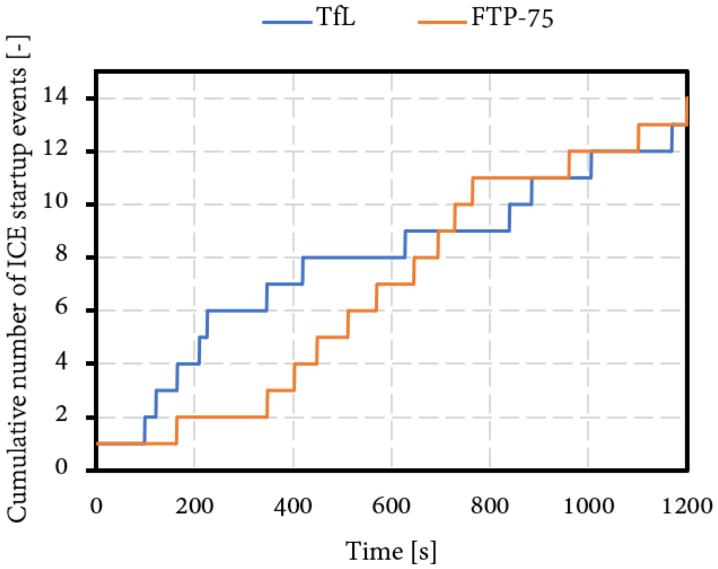

Figure 37. Number of combustion engine startup events occurring over the initial 1200 seconds of the test cycles with the highest and lowest distance-specific NH_3 emissions (TfL, FTP-75)

By 300 seconds, over the TfL cycle the vehicle had restarted its engine 6 times, compared to twice for the FTP-75. Nevertheless, during this time the quantity of NH_3 emitted over both cycles was both relatively low and broadly similar; yet the distance covered during the FTP-75 was almost 4 times

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[18] Known as the TfL cycle, this cycle was developed by Transport for London and aims to reproduce highly congested urban driving, with frequent periods of extended standstill.

[19] Known as the RTS cycle, this cycle aims to reproduce relatively demanding real-world driving conditions. Broadly similar to the WLTC, it is nevertheless shorter and covers less distance.

greater, leading to a much lower distance-specific emissions result, as reflected in the value for the entire cycle.

The low-emitting vehicle with a conventional powertrain (vehicle 47) was tested over several driving cycles, results from which are shown in Figure 38.

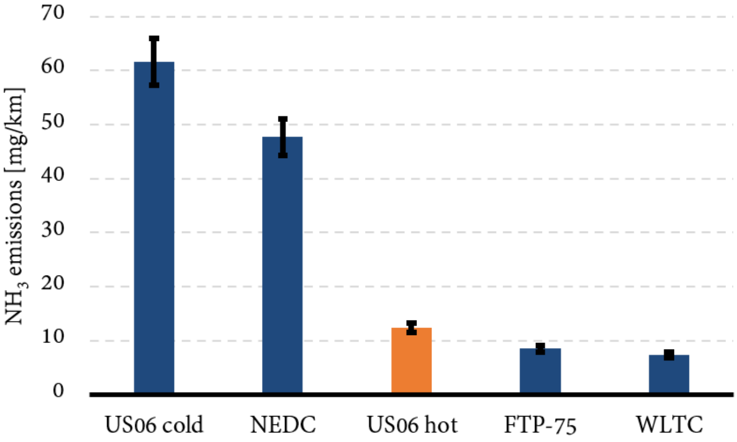

Figure 38. Results from vehicle 47 tested over 5 driving cycles (all from cold start, except for 'US06 hot', shown in orange)

As the figure shows, distance-specific emissions spanned a broad range, covering almost an order of magnitude. The fact that the US06 cold cycle showed the highest emissions is not unexpected (this test procedure is examined and discussed in the next paragraph); yet the cycle with the next highest emissions was the NEDC. These two cycles represent opposing ends of the spectrum in terms of the energy demand imposed by the speed trace and the distance travelled during the first few hundred seconds of engine operation. In the case of the NEDC, the combination of cold start, low mean speed and frequent stop events combine to cause high distance-specific emissions. This demonstrates the complex nature of multiple counteracting effects on NH_3 emissions and underlines that extrapolation (and even interpolation) based on cycle characteristics such as mean speed, energy demand, etc may not always yield satisfactory results, especially for vehicles with unusually low emissions over certain driving cycles. In the case of this vehicle, applying the previous EU type approval procedure (NEDC) lead to a result some 6.4 times lower than when applying the current procedure (WLTC).

The well-known US06 cycle (normally performed from hot start), was deployed here in variants commencing from hot and cold start. The US06 is widely recognised as being the most demanding legislative LD emissions testing procedure in any jurisdiction; for legislative testing the cycle is performed from a hot start. The cold start variant represents a deviation from US legislative requirements and an extremely demanding emissions control scenario. The hot start US06 mean NH_3 concentration was 17.4 ppm while the cold start US06 mean NH_3 concentration was 64 ppm; the resulting distance-specific gravimetric emissions were 12.4 mg/km and 61.6 mg/km, respectively. The ratio of gravimetric distance-specific emissions results for the pollutants CO, NO_x and NH_3 from three tests of this type are shown in Figure 39.

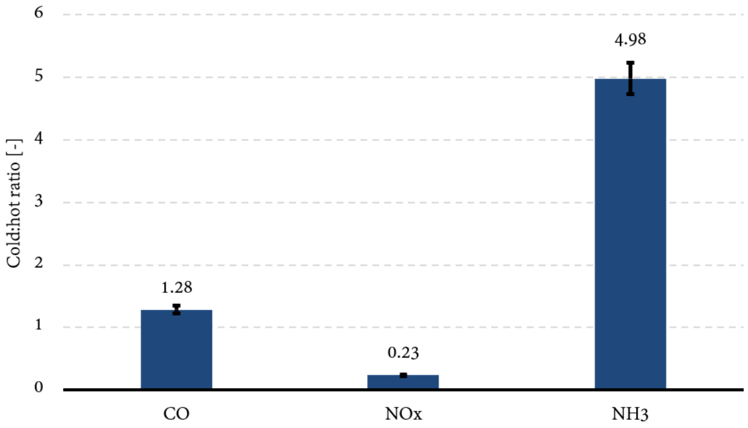

Figure 39. Ratio of gravimetric emissions results obtained from three repetitions of the US06 cold start version vs US06 hot start version

The relatively small increase in the CO emissions (just under 30%) testifies to the relatively high level of CO elimination in the aftertreatment system, notwithstanding the cold start and the extremely demanding speed trace. Despite this, the NO_x and NH_3 results show a very strong influence of the start condition: emissions of the former decreased by a factor of approximately 4; the latter increased by a factor almost 5.

The cumulative gravimetric NH_3 traces are shown in Figure 40; note the fact that the mass traces are on separate vertical axes, due to the differences in magnitude.

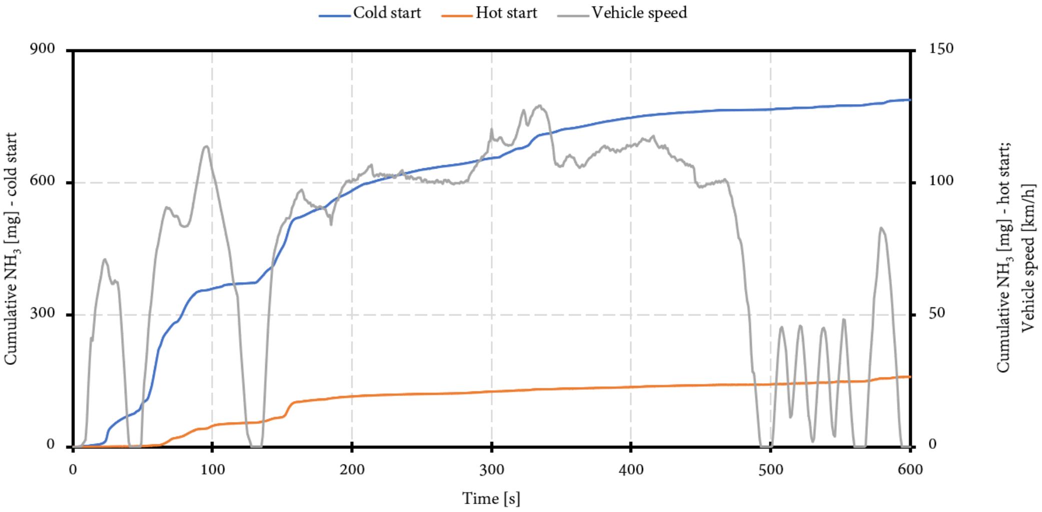

Figure 40. Cumulative gravimetric NH_3 traces over the US06 performed in hot and cold start variants for vehicle 47

In addition to the large difference in the magnitude of the cumulative emissions, the form of the traces and their relationship to the speed trace were also variable. The cold start trace shows that NH3 was detected much earlier in the cycle (~24 seconds vs ~65 seconds). The former point (cold cycle) can be assumed to roughly correspond to NO T50, but somewhat delayed due to sample transfer effects; the latter point (hot cycle) occurs just after the second, highly intensive acceleration from standstill. Consideration of the tailpipe CO emissions showed that this behaviour is primarily related to the degree of enrichment necessary to meet power demand. Both emissions traces appeared to reach a quasi-stabilised condition where the strength of the relationship between the power demand imposed by the speed trace and NH_3 emissions was much weaker. For the hot start cycle, this period commenced from around 160 seconds, while the equivalent time for the cold cycle was approximately 330 seconds.

Despite these differences in the time of onset of NH_3 emission, the proportion of the total emissions for both cycles emitted was almost identical during the period 160-200 seconds and similar during the period 200-300 seconds, as shown in Figure 41.

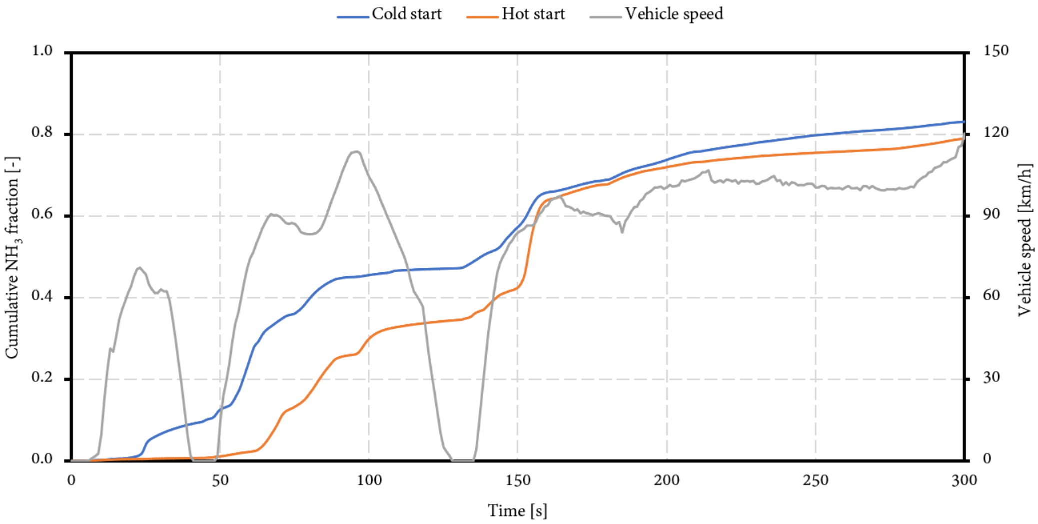

Figure 41. Normalised cumulative NH_3 emissions over the initial 300 seconds of the US06 cycle following cold and hot start for vehicle 47

By 300 seconds, around 80% of the total cycle NH_3 emissions had been emitted, regardless of the thermal start condition. By this point, the distance-specific NH_3 emissions for the cold and hot start cycles took values of 20 mg/km and 103 mg/km, respectively. At a time of 500 seconds, the NH_3 emissions following cold start had reached some 97% of their final value, while for the hot start cycle the equivalent value was just under 90%.

Results from both cycles show some behaviour suggestive of storage and release effects, with the effect being stronger in the case of the cold start cycle (as expected). However, the magnitude of this effect for the cold start cycle was more limited than expected, which may have been due to the rapid rate of engine warmup and high exhaust gas flow rate resulting from the exceptionally high power demand imposed by the speed trace. In addition to showing the strong contribution of the cold start, these results show that certain low emitters which have consistently low results over most normal driving cycles can be provoked into emitting significant quantities of NH_3 over highly demanding driving cycles such as the cold start version of the US06 (cf. [135]). Notably, despite this vehicle being the lowest non-hybrid emitter among the entire pool of 50 test vehicles, when performing the US06 from a hot start (a legal requirement in the USA – albeit one without an NH_3 limit of any kind), the reference NH_3 concentration of 10 ppm was exceeded, by some 70%. As the displacement and rated power of the vehicle's engine mean it has much in common with some HD engines, the fact that the EU HD NH_3 requirement was not met is arguably a significant finding.

5.2.4. Investigation into NH_3 emissions from low emitting vehicles under less demanding driving conditions

As a corollary to the investigations with low emitting vehicles (in the preceding section) it was investigated whether two high emitting vehicles (vehicles 2 and 10) emitted significant quantities of NH_3 when operated under vehicle operating conditions with characteristics deemed to have a very low propensity for NH_3 formation. Specifically, the conditions chosen were:

- thermally stabilised idle
- thermally stabilised driving at constant speeds of 50 and 70 km/h, in 4th and 5th gears, respectively, with normal road load simulation applied.

Thermally stabilised idle was included as a condition representing low load *in extremis*, for which no fuel enrichment is expected. Note that the stationary idle condition also makes frequent appearances in the vehicle's type approval cycle, under both warmup and hot running conditions. The non-zero speeds (and gear choices) were chosen since they occur as constant speed sections in the NEDC (the vehicles' type approval cycle) and also because they both represent driving conditions characterised by moderate load and relatively low distance-specific fuel consumption, especially for passenger cars with low displacement SI engines. For the measurement at idle, the vehicles were thoroughly warmed up by driving the entire NEDC cycle, then left at idle. After a stabilisation period of 100 seconds, the measurement period (of duration 100 seconds) commenced. For the non-stationary tests, the vehicles were in the hot start condition and were accelerated to the speed of interest. Following a period of stabilisation (100 seconds), the measurement was carried out (of duration 150 seconds), during which the driver kept the vehicle speed as constant as possible (in practice this was within approximately ±0.2 km/h at both speeds). The coefficient of variance of the measured NH_3 concentration at idle was some 2%; this increased to almost 10% for the sampling at 50 and 70 km/h, but note the fact that the variation in engine rotational speed was greater under non-stationary driving conditions than at idle.

Concentrations measured at idle (as detailed above) are shown in Table 7.

Table 7. Mean NH_3 concentrations at idle from the two high emitting vehicles

High emitting vehicle	Idle – mean NH_3 concentration at idle [ppm]
Vehicle 2	2.66
Vehicle 10	8.71

The concentrations at idle were high in the case of vehicle 2, where the concentration equates to 87% of the current HD mean concentration limit of 10 ppm. Nevertheless, vehicles with broadly similar characteristics have been reported to show NH_3 concentrations at thermally stabilised idle of some ~25 ppm [321]. The concentration at idle for high emitter 1 is only 30% that of vehicle 2, yet in view of the relatively low uncertainty of the concentration measurement (achieved via the extended sampling period and the aforementioned countermeasures regarding the zero response), it can be stated with relatively high confidence that the measured concentration significantly exceeds background levels and thus that the measurement is not an artefact. Given that the rate of fuel consumption at idle is the minimum value of all periods where the engine is fuelled, and that load at idle consists only of frictional and parasitic losses, a measured NH_3 concentration of 2-3 ppm remains noteworthy, especially in view of the fact that the concentration of NO_x in the exhaust gas of the same vehicle under such conditions were found to be almost an order of magnitude lower, typically taking values <0.5 ppm.

Results obtained under constant speed driving conditions are shown in Table 8.

Table 8. Mean NH_3 concentrations at idle and gravimetric NH_3 emissions at two constant speed driving conditions from the two high emitting vehicles

High emitting vehicle	50 km/h – mean NH_3 concentration [ppm]	Emissions at 50 km/h – [mgNH_3/km]	70 km/h – mean NH_3 concentration [ppm]	Emissions at 70 km/h – mgNH_3/km
Vehicle 2	9.73	2.21	13.46	5.61
Vehicle 10	13.79	3.14	12.12	2.69

Emissions for the stabilised non-idling driving intervals were higher than at idle, but the increase was not proportional to the increase in engine load of fuel consumption, when comparing to idle. At 70 km/h both vehicles' NH_3 concentration exceeded 10 ppm, while at 50 km/h vehicle 1 level was very close to that limit. Vehicle 2 in fact had a higher concentration at the lower of the two speeds, although the difference was of limited significance given the inherent variability in the concentration, quantified by the aforementioned value of the calculated coefficient of variance. Gravimetric emissions did not exceed 5.61 mg/km, this rather low figure resulting from the low load conditions inherent in constant speed driving at moderate speed and the corresponding strong throttling of intake air leading to a modest exhaust gas flow rate. Significantly, the gravimetric NO_x emissions for both vehicles were <1 mg/km at both of the constant speed conditions examined. (Emissions of N_2O were extremely low under all hot running conditions, regardless of engine speed or load.)

At constant speeds on the order of 50-70 km/h and with normal road load for vehicles of this type, the power developed at the wheel is modest, on the order of ~3-5 kW and the engine is operating at a low proportion of its rated power (<10%). Nevertheless, as mentioned, gravimetric NH_3 emissions were non-negligible. Table 9 shows the work-specific gravimetric NH_3 emissions for high emitters 1 and 2.

Table 9. Work-specific NH_3 emissions measured at constant speed

Vehicle	Work-specific emissions at 50 km/h [mgNH_3/kWh]	Work-specific emissions at 70 km/h [mgNH_3/kWh]
High emitter 1	2.21	5.61
High emitter 2	3.14	2.69

5.2.5. Investigation into NH_3 surges attributable to TWC light-off for the case of Euro 6 vehicles and their contribution to total cycle NH_3 emissions

The traditional view of conditions conducive to NH_3 emissions has overwhelmingly referred to periods of high load, which, in line with the so-called crescendo effect, rarely coincide with cold start powertrain operation during widely used emissions test procedures. In recent years, many assessments have highlighted the cold start/TWC light-off event as a highly significant contributor to NH_3 emissions over cold start test procedures. Self-evidently, the contribution of any driving event to total emissions over a given driving cycle is a function of the residence time of such conditions during the driving cycle. For cold start driving cycles (such as the WLTC and NEDC), the cycle commences with a cold start, followed by some driving, during which TWC light-off occurs, followed by a further range of driving conditions before the periods of highest load occur during the latter stages of the cycle. Care should be taken to distinguish between concentrations and gravimetric emissions, as well as total (gravimetric) emissions and distance-specific gravimetric emissions. In the cases of the NEDC and WLTC, the ratios of the distances covered by the cycles' respective initial (urban) phases and their final, motorway-like phases are 1.75:1 and 2.67:1, respectively.

A subset of 6 vehicles type approved to the WLTP (Euro 6) were tested over the NEDC and WLTC to address this question. The vehicles in this subset all had NH_3 emissions lying within the interquartile range of gravimetric NH_3 emissions when tested over the WLTC (Figure 29).

Figure 42 shows the distance-specific NH_3 emissions for each phase of the NEDC.

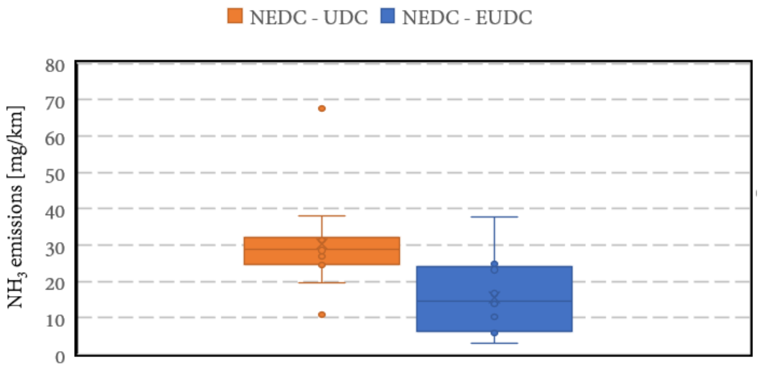

Figure 42. Distance specific NH_3 emissions for the two phases of the NEDC

All vehicles showed behaviour where the cold start and light off was characterised by substantial NH_3 emissions. In the case of the NEDC, there was some overlap in the values taken for the two phases, although the interquartile ranges almost coincided, but in fact featured no overlap. These results lend weight to the argument that urban and non-urban emissions factors should be used for modelling and calculations at the fleet level. Two vehicles were identified as outliers during the UDC phase (one high; one low), but there were no outliers for the EUDC. This appeared have be related to the strong link between TWC light-off and NH_3 emissions, as well as to the relatively high proportion of idling in the UDC – the outlier with high emissions showed substantial NH_3 emissions during all idling events except for the first two, which significantly contributed to the total emissions result for that phase. The outlier with low emissions showed very low NH_3 emissions during all periods of idling.

The NEDC's UDC phase consists of a speed trace made up of a repeating pattern of which four iterations are performed, meaning that the thermochemical evolution of the exhaust gas and its interaction with the TWC is made apparent.

Figure 43 shows distance-specific NH_3 emissions for each phase of the WLTC, obtained from the same test vehicles.

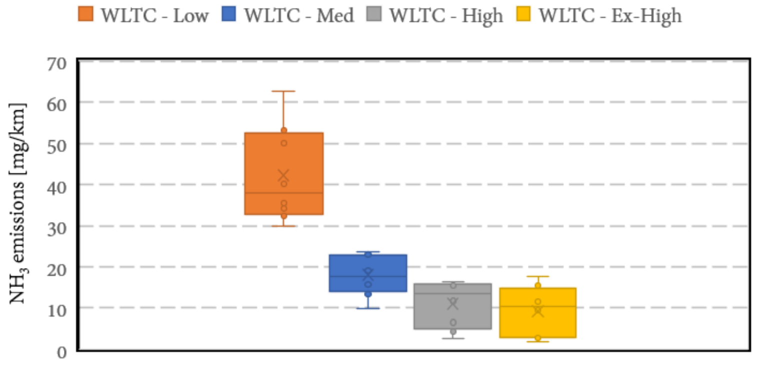

Figure 43. Distance specific NH_3 emissions for the four phases of the WLTC

For the WLTC, the distance-specific NH_3 emissions can be divided into three categories: the initial, cold start WLTC Low phase; the WLTC Medium phase; and High/Extra high phases (combined). These results strongly support the separation of different types of driving as concerns the reporting of typical fleet-level NH_3 emissions factors. The Low phase featured both the highest emissions and the greatest range, although no outliers were statistical identified by the box-and-whisker analysis. The mean and median values for that phase were close to 40 mg/km. The medium phase, which commences after almost 10 minutes of powertrain operation, featured a much smaller range and the mean and median values were some 16 mg/km. The High and Extra-High phases showed results which were very similar, with near identical mean and median values and similar ranges.

The results presented above show a clear dominance of the initial, urban driving phase, although it is to be borne in mind that that phase is also the only one to include the cold start event. The magnitude of this effect is greater during the WLTC than during the NEDC, most likely due to the differences in the proportion of idling and extended periods of constant speed driving which make up the majority of the NEDC's EUDC phase (but which do not feature in any phase of the WLTC).

A recent study – which did not make use of the NEDC – reported extremely strong dominance of the cold start effect for vehicles tested over the WLTC [27]. Data collected as described above support this to a relatively low degree and generally show closer agreement with the NH_3 profiles as reported elsewhere (e.g. [48], [321]) which generally show less compression in the time domain, with significant contributions from all 4 phases of the WLTC to the final value for the entire cycle. Nevertheless, it is noteworthy that short trips covering only a few km and consisting entirely of urban driving caused substantial NH3 emissions from these test vehicles (often ~40 mg/km), which has self-evident implications for various real-world NH_3 emissions scenarios.

5.2.6. Investigation into the impact of the so-called "crescendo effect" on NH_3 emissions during cold start test procedures

The research question addressed in this section concerns the impact of the crescendo effect in test procedures on NH_3 emissions. Practically, this was achieved by employing a modified test procedure making the TWC light-off event coincide with very low load, or making it coincide with high load. This point was investigated in three ways, using a total of two test vehicles which were known to have relatively (but not excessively) high NH_3 emissions (residing in the upper quartile of the entire fleet, as shown in Figure 29).

The first method was to significantly extend the period of initial idling to ensure that light-off of the TWC had occurred well before the first acceleration from rest – this way, TWC light off occurred under very low load conditions. Such an approach, while very rarely employed in exhaust emissions studies, may be found in the literature dealing with unregulated emissions from SI engines (a single example was found in a study reporting NH_3 measurements, namely [196]).

The baseline case was established by running the entire NEDC, with no sub-phases omitted. Figure 44 shows concentration traces from vehicle 2, showing a gradual reduction of NO and an NH_3 profile characterised by 3 surges.

When omitting sub-phases of the UDC, the emissions behaviour of both NH_3 and NO_x was substantially altered. An example of the concentration traces of NH_3 (and NO) is shown in Figure 45, again for vehicle 2.

As is evident from the concentration trace, during the first 400 seconds of idling, the concentration of NO rises to very high values, falls sharply, increases again, oscillates and falls then non-monotonically, reaching low values from around 320 s onwards. During this period, the measured concentration of NH_3 was at levels statistically indistinguishable from zero. The first acceleration (occurring at 400 s) was associated with a surge of NO, but the second acceleration was associated with a surge of NH_3. Thereafter, the NH_3 concentration was relatively stable (but did not approach zero), while the concentration of NO was low but highly variable. This lack of correlation between the two species is suggestive of gradual release of NH_3 from a storage reservoir, which appears to be facilitated by the increased exhaust gas temperature, flow rate and possibly variation in λ which results from transient driving (as opposed to idling, where those parameters are normally very stable, except immediately following cold start). The coincidence of the 2nd NH_3 surge with the acceleration to 70 km may represent more than NH_3 caused by enrichment to meet power demand – the shape of the concentration response suggests that the increased temperature and flow rate may have liberated further latent NH_3 stored on metal surfaces (as well as in accumulations of liquid water, which were finally removed by the combined effects of temperature and gas flow rate).

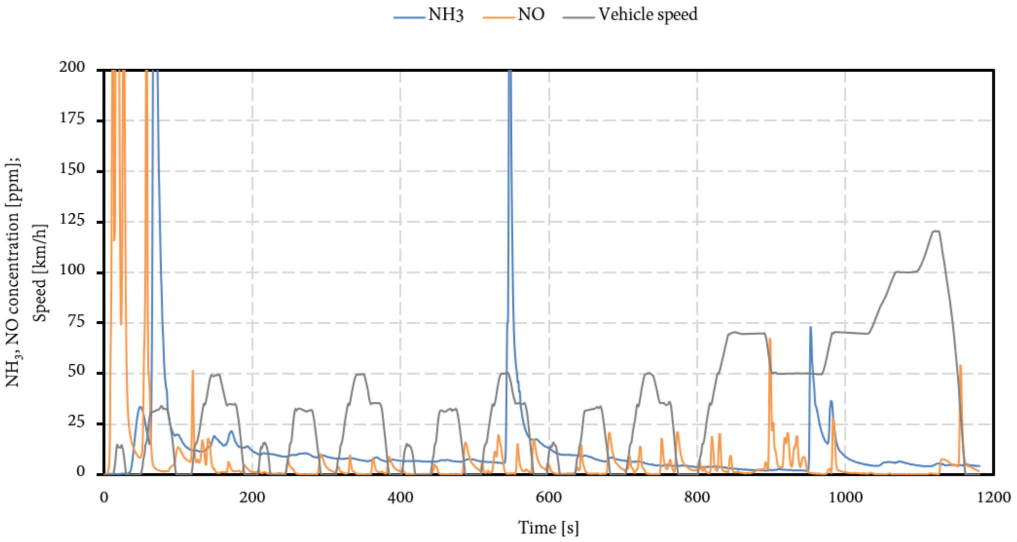

Figure 44. NH_3 and NO concentration traces over the NEDC in its unmodified form; note that the peak in NO and NH3 concentrations exceed the vertical axis at certain points

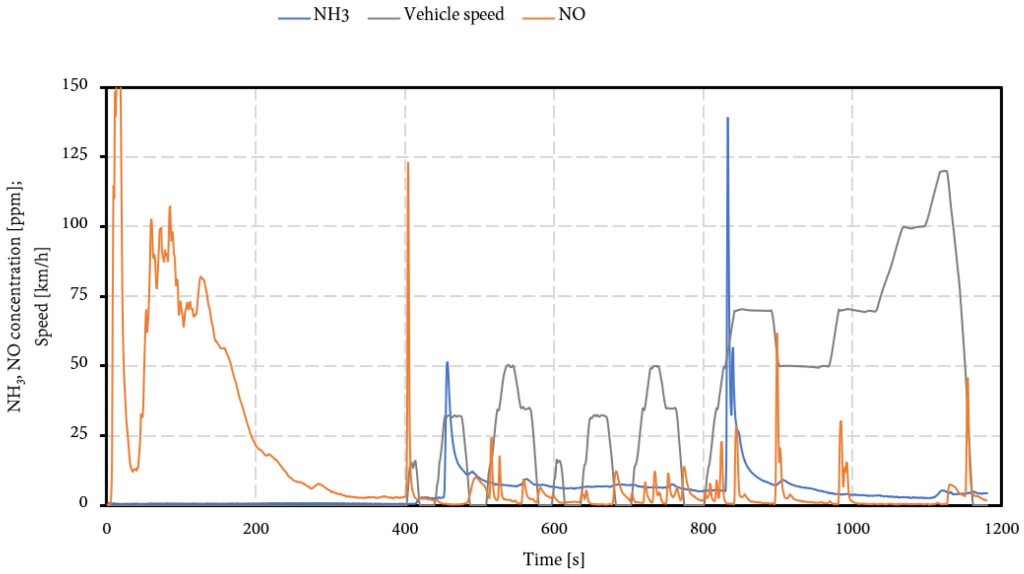

Figure 45. NH_3 and NO concentrations in the exhaust gas, measured from vehicle 2 over the NEDC, with the initial 2 sub-cycles of the UDC consisting only of idling. Note that the initial peak in NO concentrations exceeds the vertical axis

When eliminating a further iteration of the UDC, so that only one iteration was driven before the EUDC commenced, the observed trends were broadly similar, but were clearly time-shifted, as evidenced by Figure 46.

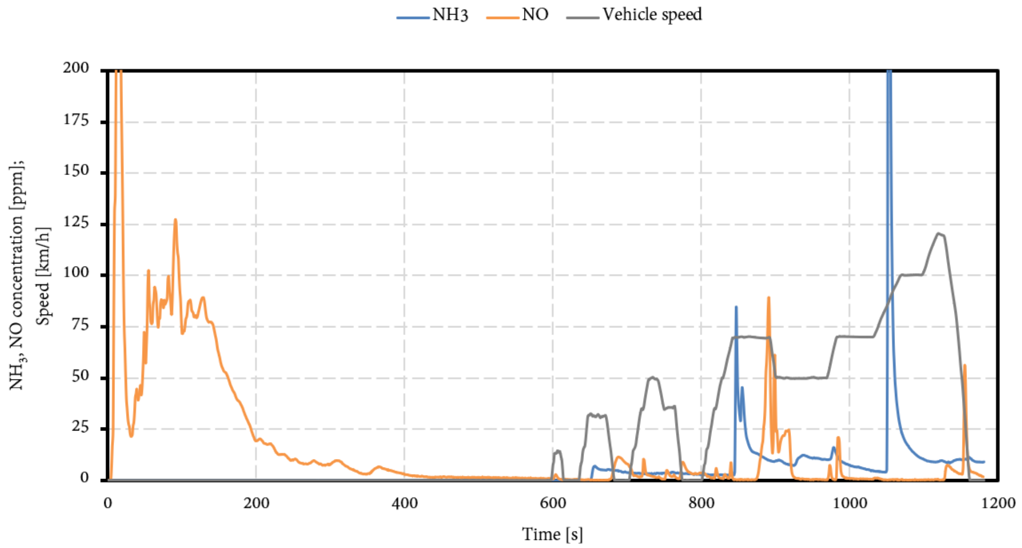

Figure 46. NH_3 and NO concentrations in the exhaust gas, measured from vehicle 2 over the NEDC, with the initial 3 sub-cycles of the UDC consisting only of idling. Note that some NO and NH_3 concentrations exceed the vertical axis.

In this case, NH_3 was first detected well after the first acceleration (in fact, at the end of the 2nd acceleration) and the concentration remained at low levels until the very end of the acceleration to 70 km/h. Again, the form of the concentration profile is suggestive of an NH_3 outgassing effect (from metal surfaces and liquid water), with the strength of the effect apparently being somewhat affected by the duration of the initial idling (cf. Figure 20).

Emissions results from the two vehicles tested in this manner are shown in Table 7.

Table 7. NH_3 emissions results from the two high emitting vehicles tested over three versions of the NEDC (1 unmodified; 2 modified versions)

Cycle version	Vehicle 2 – UDC phase NH_3 emissions [mg/km]	Vehicle 2 – EUDC phase NH_3 emissions [mg/km]	Vehicle 10 – UDC phase NH_3 emissions [mg/km]	Vehicle 10 – EUDC phase NH_3 emissions [mg/km]
Full NEDC: UDC sub-cycles 1-4+EUDC	13.7	2.4	1.6	4.2
UDC sub-cycles 3-4+EUDC	4.9	2.7	9.8	16.8
UDC sub-cycle 4+EUDC	1.7	7.8	18.4	8.8

Self-evidently, the reduced distance of the first phase for the two variants with eliminated sub-cycles affects the distance-specific results for the UDC. However, the distance covered during the EUDC is always the same (at least nominally), and yet both vehicles showed significant differences during that phase, depending on the driving profile of the proceeding phase, as shown in Figure 47 and Figure 48.

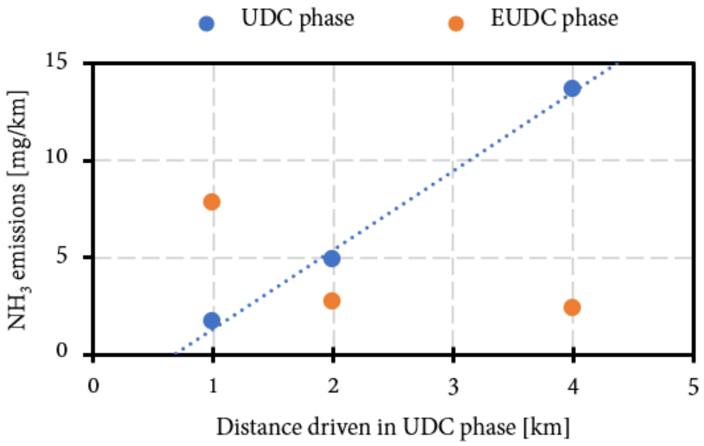

Figure 47. NH_3 emissions results from vehicle 2 tested over 3 variants of the NEDC

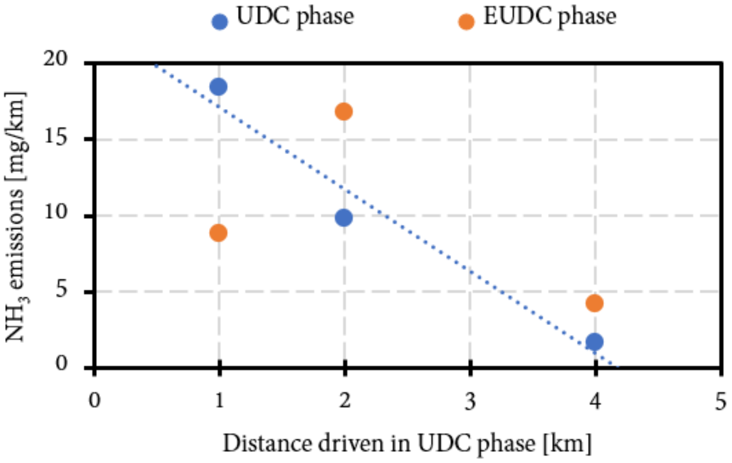

Figure 48. NH_3 emissions results from vehicle 10 tested over 3 variants of the NEDC

Surprisingly, the trends for the UDC phase are inverted for the two vehicles, despite them being of similar specification from many points of view. For vehicle 2, longer initial idling lead to lower distance-specific NH_3 emissions, despite the lower distance travelled (and thus the lower denominator, which would obviously to increase the distance-specific results). For vehicle 10 this effect was reversed; lower emissions resulted as the distance increased, but the increase in distance *per se* (i.e. alone) was not sufficient to explain the strength of the effect, as shown in Figure 49.

In conclusion, for vehicle 1 the correlation between the amount of wheel work performed and the quantity of NH3 emitted was positive and relatively strong, while for vehicle 2 the correlation was non-negative (although weak and therefore perhaps in fact non-existent).

Regarding results from the EUDC phase (refer to Figures 47 and 48), behaviour was non-linear and non-monotonic, but unsurprisingly, in both cases the lowest EUDC emissions occurred where 4 km had been driven before. Again, the explanation offered for this behaviour is one of storage and release effects, including the boiling off of water deposits – however, such an explanation would not account for the differences between the two vehicles observed in the UDC phase. Further effects responsible for this complex and variable behaviour may stem from interactions between various species involved in NH_3-forming reactions, such as NH_x intermediates and their storage on the TWC (both the PGM and the support). Another possibility relates to the powertrain control strategy and the way it reacts to extended idling before any wheel work has been performed. Further investigation of this point and equivalent testing on a broader pool of vehicles would be required to draw more concrete conclusions.

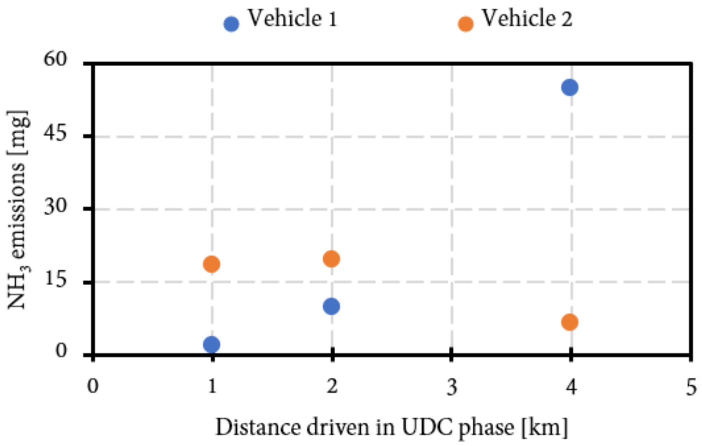

Figure 49. NH_3 emissions masses (not distance-specific) for vehicles 1 and 2 tested over the UDC phase of the 3 variants of the NEDC

The second method used to investigate the question posed in this section was to use a driving cycle which featured significantly higher load during the period where cold start effects are most significant, i.e. during the initial ~300 seconds of driving. The speed trace from the NEDC's EUDC phase was used for this purpose, with 4 iterations performed, thus yielding a cycle consisting of 4 identical sub-trips covering a total distance of 28 km, the limited idling events being separated by sub-trips of 7 km. The gravimetric NH_3 emissions and $\{NH_3\}$ values obtained from that test procedure are shown in Table 10; $\{NH_3\}$ results are also shown in Figure 50 and Figure 51.

Table 10. NH_3 results for the individual sub-cycles that make up the UDC phase of the NEDC for the high emitting vehicles

Cycle iteration	Vehicle 2 – NH_3 emissions [mg/km]	Vehicle 2 – $\{NH_3\}$ [-]	Vehicle 10 – NH_3 emissions [mg/km]	Vehicle 10 – $\{NH_3\}$ [-]
1	12.7	0.74	15.6	0.81
2	10.4	0.86	6.1	0.80
3	6.9	0.86	1.2	0.69
4	9.2	0.89	1.1	0.73

The high values taken by $\{NH_3\}$ at the very beginning of the sampling period result from small sampling artefacts – while the concentration of NO in the exhaust remains low, very low concentrations (~1 ppm) of NH_3 caused by inherent analyser uncertainty and possibly also by quantification of latent NH_3 released from metal surfaces nevertheless dominate the RNC flux, causing $\{NH_3\}$ to take high values, even approaching 1.0. However, as soon as the production of NO begins in earnest, particularly during the initial acceleration from rest, $\{NH_3\}$ remains low until NO T_{50} is reached, which occurs rapidly in this case, due to the acceleration through the gears to 70 km/h causing the exhaust gas enthalpy to be relatively high. Comparing the gravimetric emissions and the values of $\{NH_3\}$ from the four iterations, it is clear that there is no real correlation between them. The much greater emissions during the 1st iteration for vehicle 10 (compared to the other iterations) is evident from a cumulative emissions plot, as shown in Figure 52. By 470 seconds, some 84% of the total NH_3 emitted during the test had been emitted, despite having only covered around 30% of the total cycle distance.

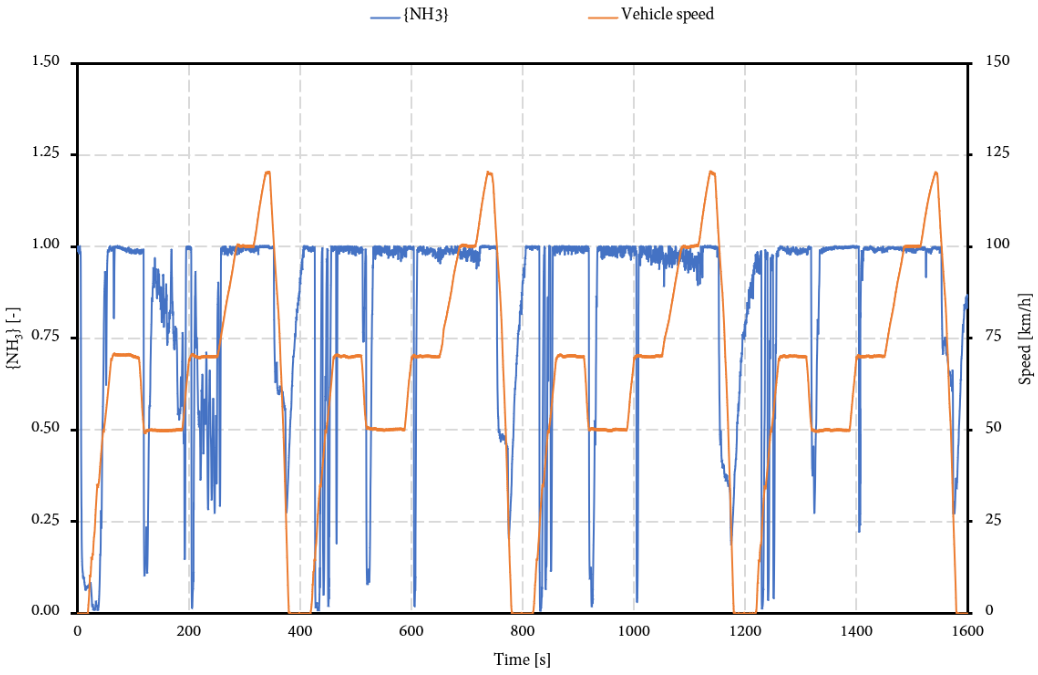

Figure 50. {NH_3} for vehicle 2 tested over 4 iterations of the EUDC cycle

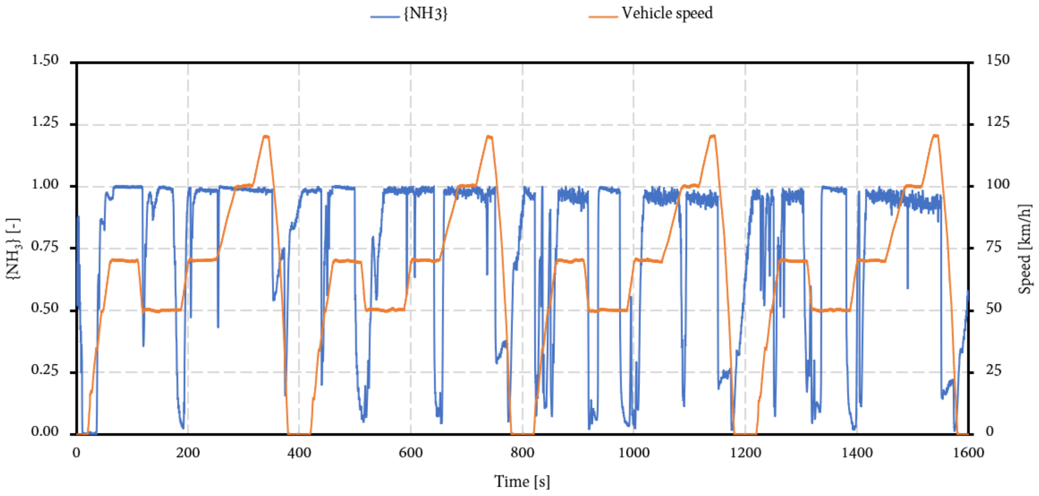

Figure 51. {NH_3} for vehicle 10 tested over 4 iterations of the EUDC cycle

A regime transition appeared to have occurred at the aforementioned point, since thereafter NH_3 emissions appeared to be in a hot stabilised regime, with the remaining kilometres/iterations causing a modest, highly linear increase in the cumulative value of NH_3 emissions, i.e. the NH_3 mass flow was relatively constant during this period. Interestingly, the behaviour for NO appeared entirely unaffected by this NH_3 regime transition – the NO-producing driving events occurring after 470 seconds coincided with low (but non-zero) NH_3 emissions, as can be seen from the cumulative mass traces for those species shown in Figure 52.

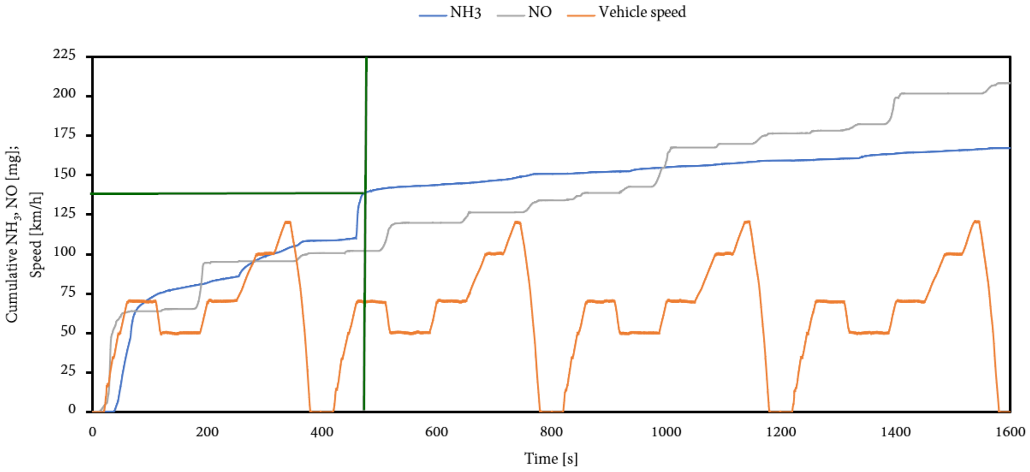

Figure 52. Cumulative NH_3 emissions obtained over 4 iterations of the EUDC from vehicle 10. Gridlines removed for clarity. The green lines are merely visual aids to emphasize the coordinates at which NH_3 regime transition occurred – refer to the text for discussion

The third method employed was to focus on the real time measurements obtained from testing vehicle 2 over 4 iterations of the NEDC's UDC phase. As mentioned in an earlier section, cold start driving cycles with non-repeating sub-units are subject to anisotropic effects, complicating the relationship between the speed trace and exhaust emissions. For the UDC, where the repeating pattern lasts 780 seconds (i.e. more than twice as long as a typical approximate cold start period of 300 seconds), a simple yet effective approach may be used for cumulative exhaust emissions, whereby the inflection point is identified by performing a linear fit backwards from the value at end of the phase, finding the first point at which the datapoint lies outside the trendline ±1 standard deviation [322]. Such an approach is shown in Figure 53 (for the example of CO emissions over the first 700 seconds of the UDC).

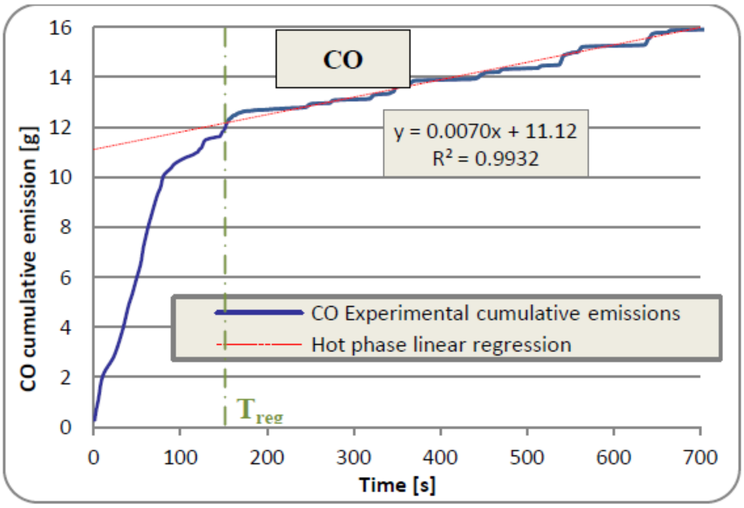

Figure 53. Literature example of a graphical approach to emissions analysis for a cold start driving cycle, shown here for the case of CO. Image source: [322]

Compare a sample NH_3 trace obtained over the UDC, as shown in Figure 54, featuring a line of best fit drawn from the right side (i.e. beginning from t = 780 s) which terminates where the cumulative NH_3 trace deviates from the line of best fit by more than 1 standard deviation [322].

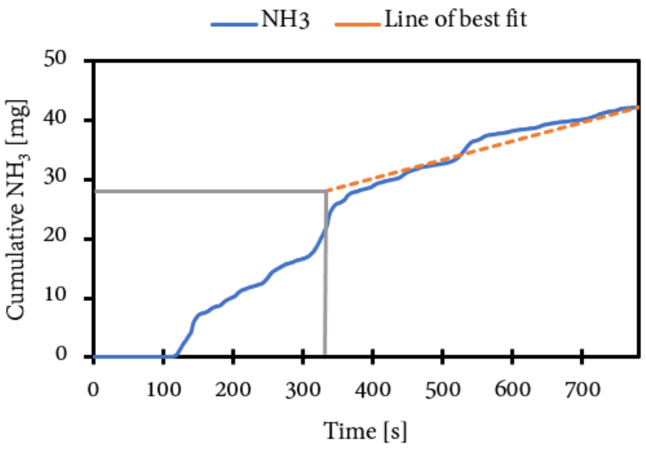

Figure 54. Cumulative NH_3 emissions over the UDC with an added line of best fit; the grey lines are visual aids

Here the deviation from the reverse (right-to-left) linear regression occurs at 330 seconds, i.e. significantly later than in the case of CO (cf. Figure 53). However, if the time at which NH_3 was first detected (first instance of concentration >2 ppm for 3 consecutive seconds) is redefined as t = 0, then the deviation occurs at 220 seconds, i.e. significantly closer to the "T_{reg}" value for CO shown in Figure 53. From this point onwards, NH_3 emissions are essentially unaffected by the cold start having previously occurred, despite the fact that at this point the powertrain has not yet achieved full thermal stabilisation, as reflected in values such as coolant and oil temperature, as well as the temperature of the exhaust gas at the tailpipe. The interpolated y-intercept of the line of best fit takes a value of around 16 mg, which can be understood as the best estimate of the magnitude of the excess NH_3 emissions not related to distance for this particular vehicle operating under these specific operating conditions.

In Figure 55 the cumulative profiles for CO and NO from the same emissions test are added. It is immediately apparent that the ongoing release of NH_3 up to the end of the sampling period (t = 780s) puts NH_3 in marked opposition to NO and CO, emissions of which essentially cease after 175 and 350 seconds, respectively.

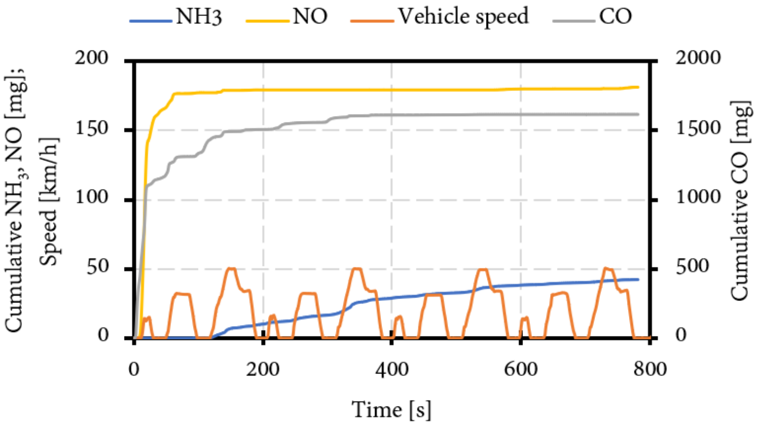

Figure 55. Cumulative emissions traces for NH_3, NO and CO for vehicle 2 over the UDC

This emphasizes the difference in behaviour for NH_3 compared to the other two species, as well as highlighting the fact that NO emissions are at very low levels following the first detection of significant levels of NH_3 in the exhaust gas. Furthermore, while NH_3 is often correlated with CO breakthrough, the figure provides an example of the general observation that substantial NH_3 emissions can occur simultaneously with negligible CO emissions. For that reason, these emissions are judged to be cold-start dependent. Note that the onset of the NH_3 mass flow is occurs very close to the point at which the cumulative NO emissions asymptotically approaching their maximum value, indicating an RNC phase transition.

The repeating units of the UDC also allow examination of the impact of cold start and warmup on the evolution of $\{NH_3\}$. Such behaviour is shown in Figure 31; note the fact that $\{NH_3\}$ is initially zero, but at around 100 seconds after cold start, rapidly rises to high values and thereafter seldom takes values < 0.75. Based on other observations, and considering the behaviour of the NO_x emissions, which were shown to be negligible from around that time onwards, it is strongly expected that further iterations of the same repeating units of the driving cycle would be characterised by equivalent – or even slightly higher – values of $\{NH_3\}$.

Each repeating sub-unit lasts 195 seconds and covers a distance of approximately 1 km. As is suggested by the values of $\{NH_3\}$ shown in Figure 56, the NH_3 emissions for each 195-second segment show significant deviations, by up to a factor of 4.25, as shown in Table 11.

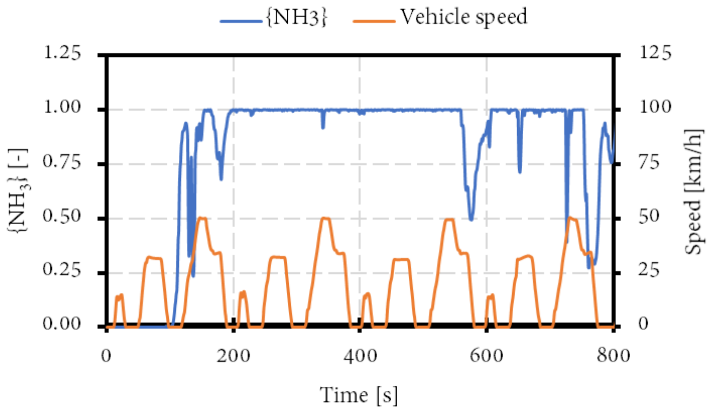

Figure 56. $\{NH_3\}$ over the UDC for vehicle 2

Table 11. NH_3 emissions over the 4 sub-cycles of the UDC for vehicle 2

Sub-cycle (195 second segment)	NH_3 emissions [mg/km]
1	9.8
2	18.7
3	9.4
4	4.4

The nature of the emissions trend means that it is not the case that shorter journeys (fewer repetitions of a given driving cycle) will always cause greater distance-specific NH_3 emissions, since very short journeys might cease before the maximum emissions rate has been achieved. For example, referring to Table 9, if the journey had terminated after 4 km, the overall emissions would be 10.6 mg/km; if the journey had terminated after 2 km the corresponding figure would be 14.3 mg/km and obviously 9.8 mg/km for the first km (alone).

5.2.7. Further investigations into correlations between NH_3 emissions and engine operating parameters for a high emitting vehicle

Vehicle 10, a relatively high emitting vehicle, was used to perform further investigations. For this purpose, exhaust emissions were measured upstream of the TWC, at the Pre-TWC sampling point. These measurements were of regulated exhaust emissions and did not include quantification of NH_3. Of particular interest was the relationship between λ and NH_3; this parameter was measured by means of exhaust gas analysis of the pre-TWC sample, which was validated against the λ value reported by the vehicle's ECU (itself based on a sensor measurement). Later, post-cat emissions were also measured and the derived post-cat λ value was also made use of, as described later in this section.

The datapoints derived from the raw measurement results (λ, NH_3 concentration) obtained over the WLTC are shown in Figure 57.

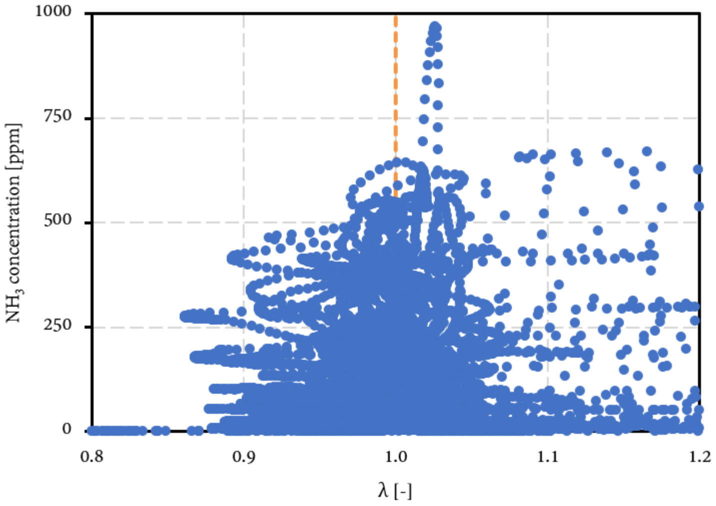

Figure 57. Measured NH_3 concentrations from vehicle 2 running over the WLTC as a function of λ, with only the base NH_3 concentration delay applied

Three points about the distribution of the datapoints in Figure 57 are potentially surprising. First, many datapoints representing non-zero NH_3 concentrations occur at high values of λ, where significant excess oxygen will be present in the exhaust gas. The likely cause of this phenomenon is the much shorter timescale over which λ varies (and over which changes in λ can be quantified), in comparison to the total response time of NH_3 analyser, which is on the order of seconds. Secondly, the lowest values of λ (<0.86) are associated exclusively with NH_3 concentrations at a level very close to 0 ppm. This is in fact due to the cold start nature of the cycle and the fact that such levels of enrichment occur only during the first few seconds of engine operation, during which time the TWC's temperature is too low to permit the formation of any NH_3. The third point is that overall there is relatively little evidence of any significant bias towards increased NH_3 concentrations at λ values < 1.0; λ values in the range 1.1–1.2 are sometimes correlated with NH_3 concentrations of several hundred ppm – and the maximum concentrations measured occur at λ values somewhat > 1 (approximately 1.03). These observations would appear to be in strong contradiction of the literature consensus on the fundamental relationship between TWC-facilitated formation of NH_3 and λ and thus it is necessary to consider the potential impact of confounding factors and potential strategies for their mitigation. The initial (base) time-shift applied to the NH_3 concentration data in Figure 32 (here defined as 0 s) had been determined previously determined based on consideration of the physical transfer time of the gas sample to the analyser's measuring cell, based on the known sample flowrate and the path length, increased by a uniform value to account for analyser response time, determined experimentally during analyser commissioning using an NO-N_2 gas mixture as the tracer species.

The impact of increasing the delay time on the value taken for the maximum measured instantaneous concentration is shown in Table 12 and in Figure 58.

Table 12. The impact of the application of additional sample transfer delay times on the pre-TWC λ value occurring for the maximum measured NH_3 concentration

Additional NH_3 delay time applied [s]	λ value for maximum NH_3 concentration [–]
0.0	1.026
1.0	1.018
2.0	1.003
2.5	0.994
3.0	0.990
3.5	0.981
4.0	0.975
4.5	0.970
5.0	0.966
5.5	0.967
6.0	0.977
7.0	0.977
8.0	1.001
9.0	1.003
10.0	1.004

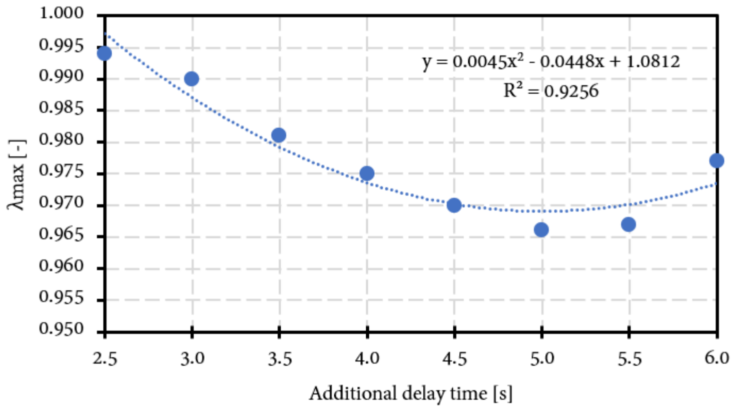

Figure 58. Graphical representation of the impact of increasing delay time on the λ value for maximum measured NH_3 concentration, for the range 2.5–6.0 seconds (refer to Table 12)

As the table and figure show, the to the nearest half-second, the lowest value of λ obtained was with an additional delay time of 5.0 seconds. Figure 59 and Figure 60 show the distribution of concentrations as a function of λ, with the aforementioned additional delay time of 5.0 s applied.

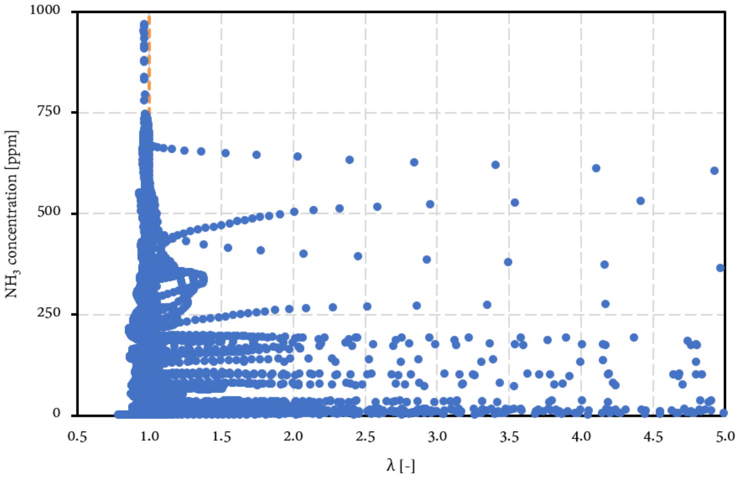

Figure 59. Measured NH_3 concentrations as a function of λ within the range 0.5-5.0, with an additional NH_3 concentration delay time of 5.0 s applied (the orange dashed line represents stoichiometry)

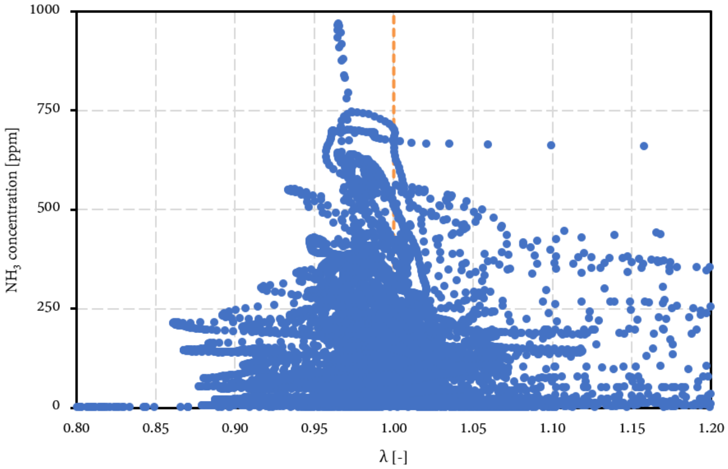

Figure 60. Measured NH_3 concentrations as a function of λ within the range 0.8–1.2, with an additional NH_3 concentration delay time of 5.0 s applied (the orange dashed line represents stoichiometry)

As the figures show, the lowest value of λ taken by any datapoint with an NH_3 concentration significantly above 0 ppm was 0.863; this characteristic lower boundary was essentially unaffected by the application of the additional delay time, since the equivalent value with no additional delay applied was 0.862.

A fundamental limitation of such an approach is that only a single, constant delay time can be applied to a concentration vector, whereas the anisotropic and strongly temperature-dependent NH_3 sample transfer delay effects occurring via absorption and condensation mechanisms are eminently not quantifiable in terms of a single value for a characteristic sample transport delay time. Furthermore, while storage is usually assumed to occur rapidly, release is likely to take place on longer timescales, especially in light of the fact that temperature – which increases during a cold start driving cycle, but usually not monotonically – is one of the controlling factors.

As CO breakthrough is normally strongly correlated with λ (unless simultaneously accompanied by NO_x breakthrough) and as CO breakthrough has been identified as a good proxy for NH_3 emissions, especially under hot running conditions [136], the CO elimination effectiveness of the TWC is of eminent interest when examining instantaneous NH_3 emissions (and the concentrations of that species). Those two results are plotted in Figure 61.

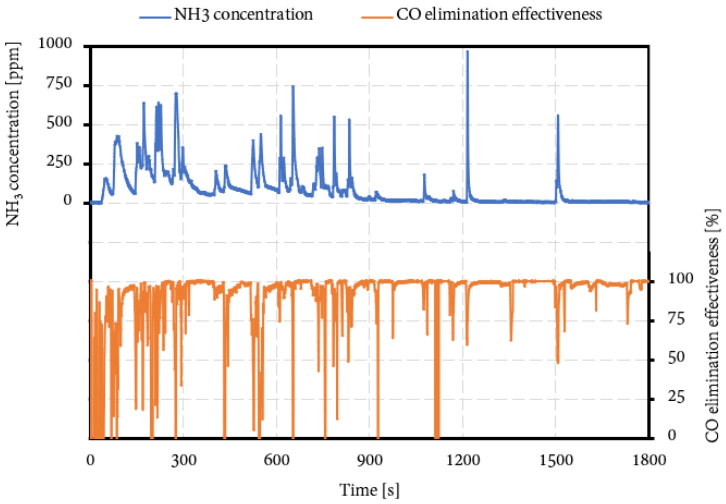

Figure 61. NH_3 concentration and calculated TWC CO elimination effectiveness

The latter portions of the cycle show a general (but not universal) synchronicity between surges in the NH_3 concentration and sudden decreases in the CO elimination effectiveness. While the overall correlation between the two parameters is of potential significance ($R^2 = 0.584$), not every deviation of the CO elimination effectiveness from values close to 100% is accompanied by a surge in NH_3 formation, as shown for a selected period of the cycle in Figure 62. For the period shown (1200–1700 s), the temperature of the TWC ranged between and 560°C and 760°C, with a mean value of 648°C and a coefficient of variance of some 9%.

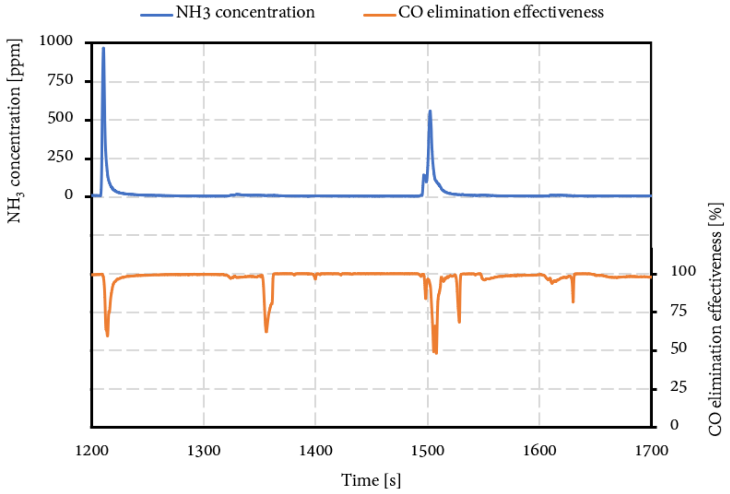

Figure 62. NH_3 concentration as a function of measured CO elimination effectiveness for a selected portion of the test

The overall correlation between NH_3 concentration and λ was found to be essentially non-existent ($R^2 \approx 0$), since the relationship is distorted by the co-occurrence of non-negligible NH_3 concentrations during periods of fuel cut-off, as well as the lack of NH_3 formation at the very beginning of the cycle (where λ takes values < 1 but NH_3 formation has not yet commenced due to the low temperature of the TWC). As periods of low CO elimination effectiveness (termed ‘CO breakthrough’) register as reduced post-TWC λ values, the post-TWC λ values were co-plotted against the NH_3 concentration, as shown in Figure 63.

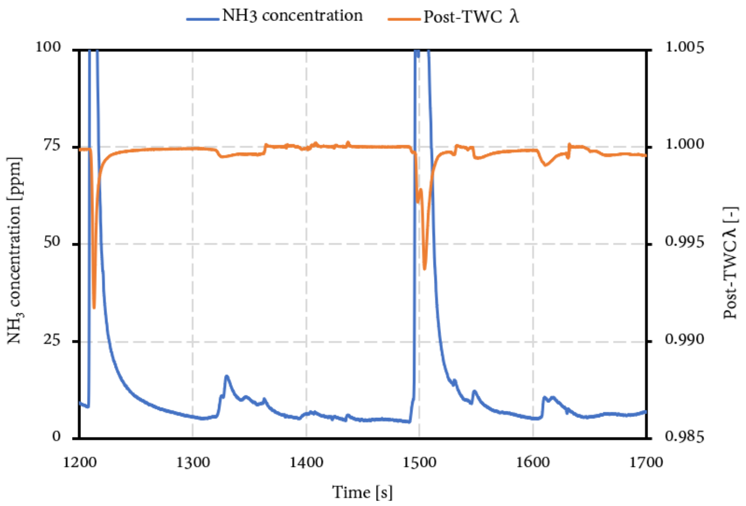

Figure 63. NH_3 concentration as a function of measured post-TWC λ for a selected portion of the test

As the figure shows, during this period deviations from stoichiometric combustion (rich excursions) result in substantial increases in the NH_3 concentration (which in this case exceed the vertical scale – refer to Figure 62). However, the NH_3 concentration never reached a value of 0 ppm, even following several seconds' operation at $\lambda = 1$. A tendency for periods of $\lambda = 1$ to be accompanied by an apparently asymptotic decrease in the measured NH_3 concentration is evident, although the usual observations relating to storage and release effects remain relevant (notwithstanding the high temperature of the entire exhaust line at this point in the cycle). While λ excursions to values < 0.995 cause large surges in the NH_3 concentration, the relationship between the value of λ and the resulting NH_3 concentration is non-linear and is complicated by a further effect: the duration of the excursion. In order to account for both the degree and the duration of the λ excursion, it was hypothesized that integrating the area under the line representing post-TWC stoichiometry (i.e. $\lambda = 1$) might yield a metric showing a more direct correlation with the associated NH_3 concentration. However, the data available were judged to be of insufficient temporal resolution to allow such an operation to be performed in such a manner that they would have produced a meaningful result.

As can be observed from Figure 63, rich excursions of limited magnitude (i.e. $\lambda \sim 0.999$) are sufficient to cause the NH_3 concentration to increase somewhat and reverse the aforementioned monotonic decrease. The implication of this is that if the measured post-TWC λ value had remained at a value of 1.0, that the NH_3 concentration might have approached a value of 0 ppm. It was decided to investigate this behaviour by running a constant speed version of the cycle, which is presented in the next paragraph.

As a final investigation, a heavily modified version of the WLTC was performed on vehicle 10. This involved transforming each phase of the WLTC into a constant speed sub-trip, as shown in Figure 64. The period of idling at the beginning and end of each phase remained unchanged, but the speed trace was altered so that the trace was followed up to the point where the mean phase speed was reached, at which point speed was made constant until such time as deceleration was required in order to perform the idling at the end of the phase according to the normal WLTC speed trace. Gear selection for the constant speed sections was performed according to the WLTP method, i.e. by specifying the highest gear for which engine speed exceeded the minimum permitted value for that parameter. For this particular test vehicle, the gears used for the constant speed sections of the four phases were 2nd, 4th, 5th and 6th, in that order.

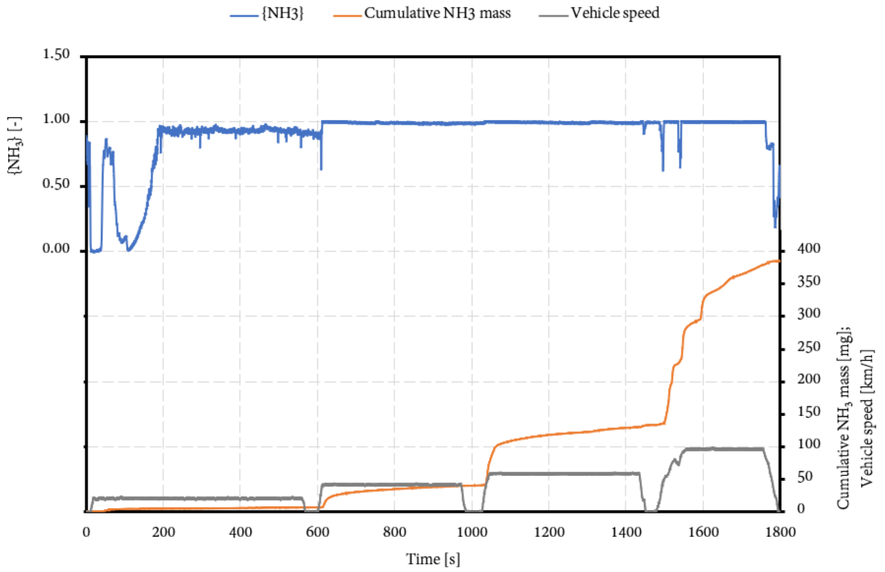

Figure 64. $\{NH_3\}$ and cumulative NH_3 mass obtained over a heavily modified version of the WLTC consisting mostly of constant speed driving

The four constant-speed phases (each of which feature only a single acceleration from rest and whose speeds increase monotonically, as shown in Figure 64) caused a very wide range of rates of NH_3 emission. Emissions predominantly occurred in two diverse regimes regarding the behaviour of the values taken by $\{NH_3\}$. Over the entire cycle, the distance-specific emissions were 16.7 mg/km, yet the first phase had cumulative NH_3 emissions of only 3 mg, i.e. < 1 mg/km. This value is despite the fact that that phase, which lasts almost 10 minutes, is conducted from cold start and includes the vast majority of the powertrain warmup period, and also despite it being characterised by a relatively high mean $\{NH_3\}$ value of 0.74. As Figure 64 shows, this phase was characterised by rather unstable values of $\{NH_3\}$, which, following TWC light off and an interruption due to the formation and release of some N_2O, oscillated within a relatively narrow range around the value 0.95; no instances of $\{NH_3\}$ approaching a value of 1.0 were observed. As constant speed was rather hard to achieve when driving at this speed in 2nd gear, the resulting fluctuations in the throttle position likely account for the majority of this instability in the value of $\{NH_3\}$. Further phases featured higher speeds, the use of higher gears and thus higher load, resulting in lower inherent variation in engine speed. The values taken by $\{NH_3\}$ were thus both somewhat higher and much more stable, defaulting to values very close to 1.0, i.e. NO_x emissions essentially ceased and NH_3 was the only RNC species present at meaningful levels in the exhaust. There were only limited departures from this, attributable to the fuel cut-off events occurring during decelerations and gear shifts during accelerations. The 2nd and 3rd phases showed similar tendencies to each other – the initial acceleration was associated with significant NH_3 emissions, but thereafter the rate of release was near-constant and relatively modest. The asymptotic behaviour observed would be suggestive of the gradual release of NH_3, although the occurrence of this effect is somewhat surprising for this portion of the cycle, since after some 600 seconds' engine operation the temperature of the entire exhaust line should be sufficient to preclude the presence of significant quantities of liquid water. Nevertheless, increased temperature is known to make the release of adsorbed NH_3 more energetically favourable and thus the increase in exhaust gas temperature resulting from the accelerations at the beginning of the 2nd and 3rd phases may have released previously stored NH_3 via such an effect. Compare, however, the aforementioned tendency for stable engine operation to allow the

NH_3 concentration to approach zero asymptotically (refer to Figure 38). The outgassing effect may have occurred at the beginning of the 4th phase, but the asymptotic trend observed in the 2nd and 3rd phases is not evident, since the acceleration event itself caused substantial NH_3 emissions, but NH_3 emissions continued during the constant speed section, showing an eminently non-asymptotic trend. In fact, it is clear that the majority of the NH_3 emitted during the cycle was emitted during the final phase, for which load was highest and for which cumulative emissions did not increase asymptotically. Note that this behaviour is almost the direct opposite of the emissions behaviour shown for the normal version of the WLTC, i.e. strong dominance of distance-specific NH_3 results for the 1st, Low phase (refer to Figure 43), despite this modified version of the WLTC also commencing from cold start and covering the same total distance.

5.2.8.Investigation into battery state of charge and powertrain warmup effects on NH_3 emissions from full hybrids tested over the WLTC

As mentioned previously, the emissions produced by vehicles with hybrid powertrains during engine restart events are of particular interest and the question as to whether there is any evidence of a clear impact of engine restart from vehicles with hybrid powertrains on NH_3 emissions is a highly pertinent one. This point was investigated by performing extended chassis dyno testing of two vehicles. The first vehicle was a non-plugin hybrid (vehicle 49), which was tested over two iterations of the WLTP. The vehicle's battery was neither purposefully charged nor discharged before starting the test; the preconditioning procedure employed was simply to run one iteration of the WLTC ~20 hours before the test commenced. The two iterations of the WLTC performed comprise a total of 8 test phase results, which can be directly compared, as shown in Figure 65.

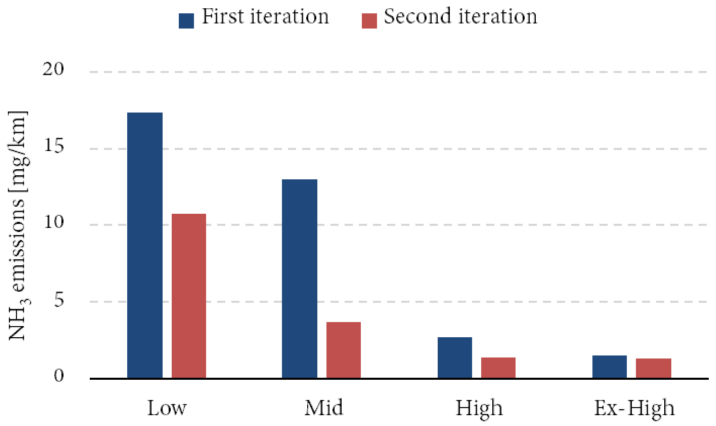

Figure 65. NH_3 results per phase obtained over 2 iterations of the WLTC

The distance-specific emissions can be divided into two broad categories: > 10 km/km and < 4 mg/km. The former occurred for the first two phases of the first (cold start) iteration and the first phase of the second (hot start) iteration. The lower emissions occur during the phases where vehicle speed and demand for wheel power is higher and the combustion engine works more frequently; for the High phase the difference is of limited significance and for Extra-high phase the observed difference is well within the calculated margin of experimental error. Significantly, the first phase of the second iteration featured NH_3 emissions > 10 mg/km, despite having completed the first iteration of the WLTC (23.3 km) only some 14 minutes previously. This somewhat surprising observation may have been related to the number of idling periods and engine restart events – recall that the 2nd, 3rd and 4th phases of the WLTC each consist of a single sub-trip only, with limited idling between the phases.

Examination of instantaneous measured concentrations of NH_3 is enhanced by data on the powertrain state of operation – i.e. whether the combustion engine is running or not. A very simple yet highly effective proxy for this is the concentration of CO_2 in the diluted exhaust gas stream, which quickly falls to background levels (~0.04 %) as soon as fuel cut-off occurs. The concentration trace shown in Figure 66 shows several interesting features, including a significant surge associated with TWC light-off, with concentrations reaching values of over 500 ppm. Furthermore, the measured concentrations persisted at relatively high levels, even tens of seconds after the diluted CO_2 concentration had fallen to background levels (i.e. after fuel cut-off). Due to the method used for calculation of the flow rate, which is based on the concentration of diluted CO_2, the aforementioned periods where NH_3 was measured while the combustion engine was not being fuelled are for the most part negated, since the near-zero flow rate that results from the aforementioned calculation leads to very low calculated mass flow values, even where the measured NH_3 concentration is relatively high (e.g. ~30–60 ppm for the period 300–400 seconds, as shown in Figure 66; compare the same period in Figure 67).

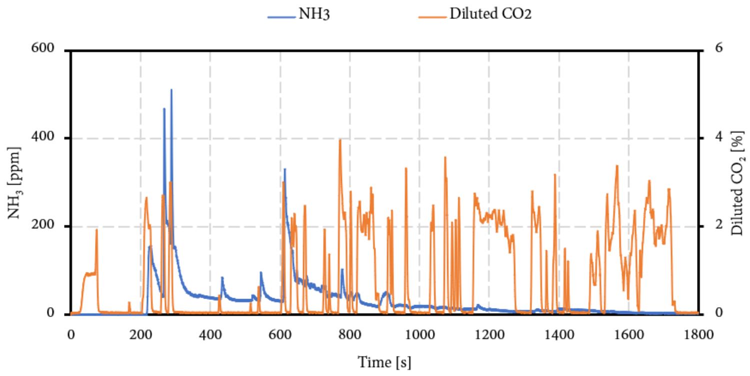

Figure 66. NH_3 (undiluted) and CO_2 (diluted) concentration traces over the WLTC

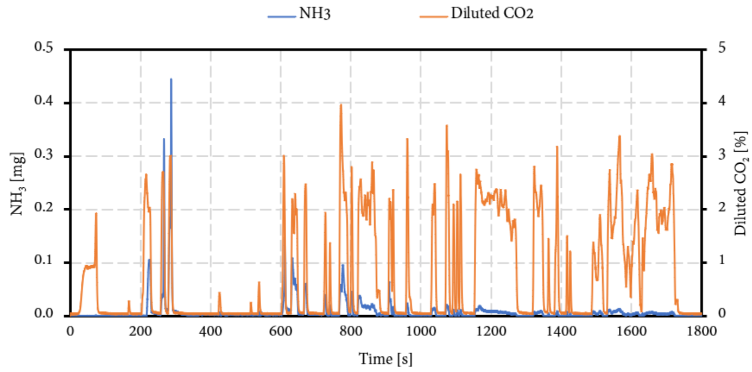

Figure 67. NH_3 emissions (undiluted, gravimetric) and CO_2 (diluted) concentration traces over the WLTC

As Figures 66 and 67 show, the engine restart events correlated to a degree with surges in NH_3 emissions, but it is important to focus on the NH_3 mass flow, rather than the concentration itself, because of the aforementioned phantom emissions effect, which is intensified – at least somewhat – by ammonia's inherent properties (stickiness, hydrophilicity). The NH_3 emissions associated with these events were of limited magnitude after approximately 1300 seconds, by which time sufficient combustion engine operating time had been accumulated to cause the apparent cessation of cold start effects. The engine oil temperature was not measured, but the inevitable warm up of the engine and its lubricant and the resulting reduction in frictional load and significant increase in the representative temperature of the combustion chamber reduces the need for excess fuelling to achieve engine startup. Notwithstanding the relatively high power demand caused by the speed trace in the range ~1300–1800 seconds, neither engine restart itself, nor sustained engine operation resulted in significant NH_3 emissions during this period. Under such conditions, enrichment is expected to be limited, due to the high temperature the engine and its fluids have reached; furthermore, the temperature of the TWC is likely to be high enough to moderate its selectivity towards NH_3, including via availability of OSC. In the context of a hybrid powertrain, it is relevant to consider that a fully warmed up TWC cools very slowly in the absence of through flow of air. If the combustion engine is rotating under fuel cut-off conditions, the aforementioned effect will occur, but under normal driving conditions this is not experienced by a full hybrid powertrain. The lack of gas flow through the TWC means that the reduction in temperature occurs slowly; significant radiative losses occur, as the TWC and its metal canning is normally at a temperature hundreds of Kelvin higher than the surrounding air; however, natural (unforced) convection is essentially negligible [323]. (It is worth noting here that in real-world scenarios, extended downhill driving of vehicles with non-hybrid powertrains can cause significant aftertreatment system cooling [324].)

The second vehicle tested was a plug-in hybrid vehicle (vehicle 50). In the first test type performed, this vehicle was tested over 4 iterations of the entire WLTP. Two tests were performed, targeting two divergent states of the traction battery's SOC (and thus the proportion of operating time for the combustion engine). In the fully charged condition, the vehicle's traction battery had a SOC of 100% at the start of the first iteration; in the low SOC start condition, the traction battery SOC was the value which the powertrain naturally reached following 4 iterations of the WLTC (i.e. the previous test, commencing from SOC = 100%). This charge sustaining SOC value was not a the minimum value occurring at any point during the WLTC, since the deceleration to standstill at the end of the 4th phase provides an opportunity to recuperate significant amounts of kinetic energy and thereby increase the SOC somewhat.

The distance-specific NH_3 emissions measured as described above are shown in Figure 68.

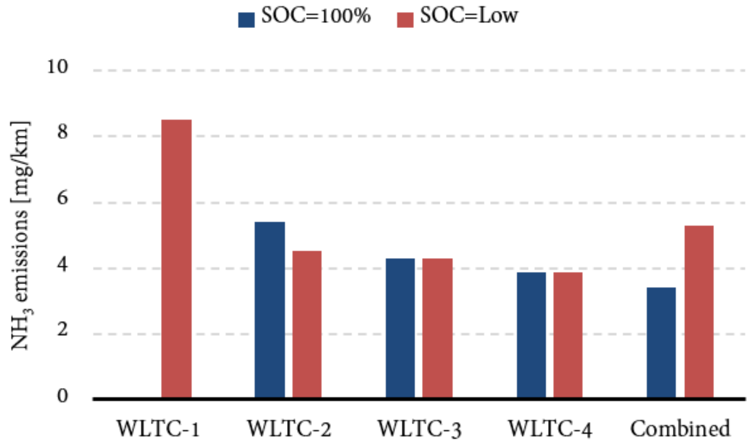

Figure 68. NH_3 emissions obtained over 4 iterations of the WLTC under two start conditions (SOC = = 100%; SOC = low)

For the SOC = 100% condition, the combustion engine did not run at all during the first iteration and the extremely low concentrations of NH_3 measured resulted only from analyser uncertainty. The iteration (and indeed the cycle phase) in which the combustion engine starts for the first time is characterised by the highest peaks in NH_3 concentrations and as a result the highest distance-specific emissions of NH_3. This observation explains the small difference between the results for the two SOC levels for WLTC-2; at the low SOC condition the engine had already been used extensively in the previous iteration, causing the cold start NH_3 contribution to be diminished. For the third and fourth iterations, no significant differences were observable in the emissions levels, which can be explained in terms of the proportion of engine operating time occurring in those cycles (having already driven almost 47 km). The small yet possibly consistent differences in the NH_3 results between the 3rd and 4th iterations (some 11%) may be attributable to the reduced fuel consumption resulting from full warmup of the lubricating oil being achieved, as well as small reductions in friction achieved by extended driving, such as full thermal stabilisation of the tyres and all bearings. An alternative – or indeed further – explanation would be a slight increase in TWC temperature reducing the selectivity towards NH_3. As a final point, it should be noted that the entire 93 km trip caused NH_3 emissions < 6 mg/km for both SOC conditions, while for the 1st iteration (23 km), the low SOC condition caused NH_3 emissions < 9 mg/km. Thus, emissions did not exceed 10 mg/km under any of the combinations tested, including the worst case scenario (low SOC, cold start). While low, the aforementioned gravimetric emissions factors are for the most part noticeably higher than the NO_x emissions for this test vehicle (and other, similar vehicles) when tested according to such a procedure.

A further plug-in hybrid vehicle (vehicle 51) was also tested. In order to investigate a broader range of and initial conditions (i.e. SOC values), this vehicle was tested in an intermediate SOC condition. The test vehicle's inertia was also increased by 75 kg beyond the value required according to the WLTP test mass definition, broadly equivalent to adding a further adult passenger to the vehicle. The increased road load and increased inertia increased the energy demand of the WLTC by approximately 8%. The targeted SOC state was achieved by charging the vehicle to 100% SOC, and then running three iterations of the WLTC's Low phase, giving a total distance of 9.3 km of urban driving of mean speed performed using exclusively electrical propulsion (since the ICE did not start at any point). Following that preconditioning, the vehicle was soaked for around 16 hours, with no charging performed, and then tested over 3 iterations of the full WLTC. Under these conditions, the ICE did not start at all during the first WLTC and started at around 2600 seconds (during the 2nd iteration). Noteworthy concentrations of NH_3 in the exhaust gas appeared soon thereafter; a total of 5.7 mg of NH_3 was measured during the remainder of the test, as shown in Figure 69.

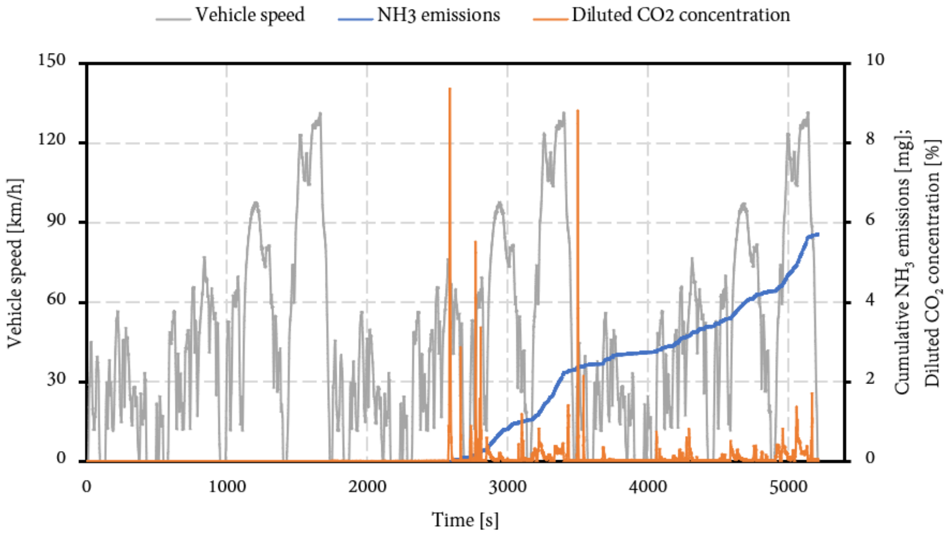

Figure 69. NH_3 emissions and the concentration of CO_2 measured in the diluted exhaust gas mixture for vehicle 51, tested over 3 iterations of the WLTC

Since no significant NH_3 or CO_2 emissions were detected until around 2600 seconds, Figure 70 focuses on the portion of the test occurring after the first startup of the ICE.

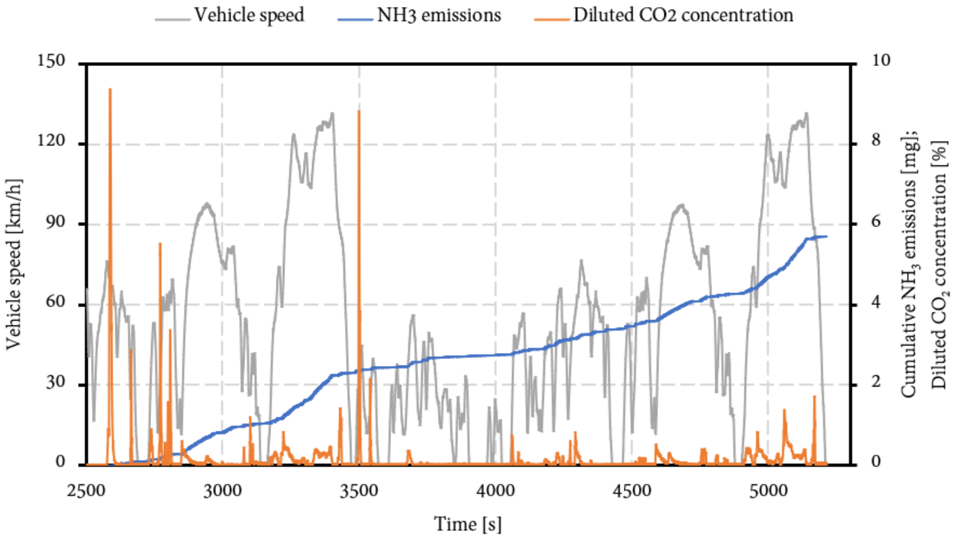

Figure 70. NH_3 emissions and the concentration of CO_2 measured in the diluted exhaust gas mixture for vehicle 51, from 2500 seconds onwards

During this portion of the test, from the initial start of the ICE to the end of the final (3rd) iteration of the WLTC, the total distance covered was 41 km, giving distance-specific gravimetric NH_3 emissions of only 0.14 mg/km. The cumulative distance-specific gravimetric NH_3 emissions are shown in Figure 71.

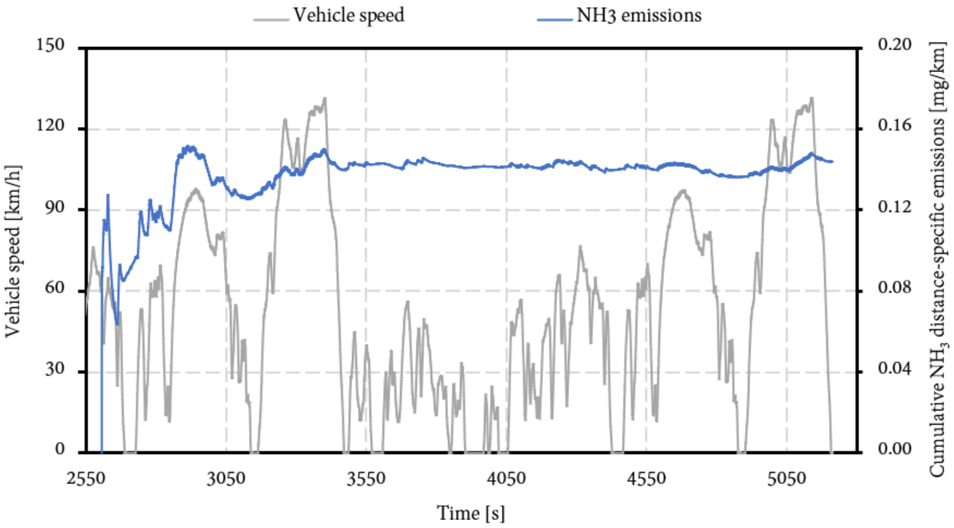

Figure 71. Cumulative distance-specific NH_3 for vehicle 51, from 2550 seconds onwards

As evidenced by Figure 71, the initial period of ICE operation is characterised by variable distance-specific NH_3 emissions, which increase gradually and non-monotonically. After around 3200 seconds onwards, by which point the ICE has been restarted several times and has accrued significant operating time, the emissions behaviour stabilises, thereafter taking values within a very narrow range, centred on a value of ~0.14 mg/km. Thus, this particular vehicle showed very low distance-specific NH_3 emissions over repeated iterations of the WLTC, regardless of the powertrain's thermal state or the driving conditions (at least within the range of driving conditions represented in the cycle). Notwithstanding the frequent ICE restart events, distance-specific NH_3 emissions were very low.

5.2.9. Investigations into NH_3 emissions from a HD CNG engine

Investigation into the NO_x-NH_3 trade-off theory and the extent to which it is supported by legislative emissions measurements of those species during the legislative type approval procedure

As mentioned previously, experiments were conducted to characterise NH_3 emissions from a single powertrain designed to run on CNG and type approved as such, according to EU HD requirements. The test powertrain was tested using the same test procedure and the same fuel, but two different control strategies. One control strategy (termed Calibration 1) was designed to meet somewhat less demanding emissions requirements and be slightly more fuel efficient, while the other (Calibration 2) was designed to meet all applicable Euro VI limits. The legislative WHTC procedure was employed (cold and hot start versions, with weighting of the results obtained from the two tests as per the legislation). Except where noted below, all applicable Euro VI emissions limits were met during all tests conducted on both calibrations.

Legislative results for the RNC species limited in Euro VI legislation (NO_x, NH_3) are shown in Figure 72, Figure 73 and Figure 74.

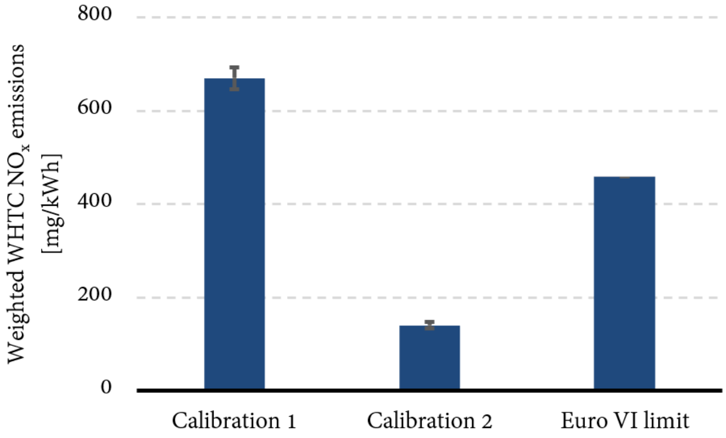

Figure 72. Legislative (work-specific, weighted) NO_x emissions for the two calibrations tested, with the applicable Euro VI NO_x limit

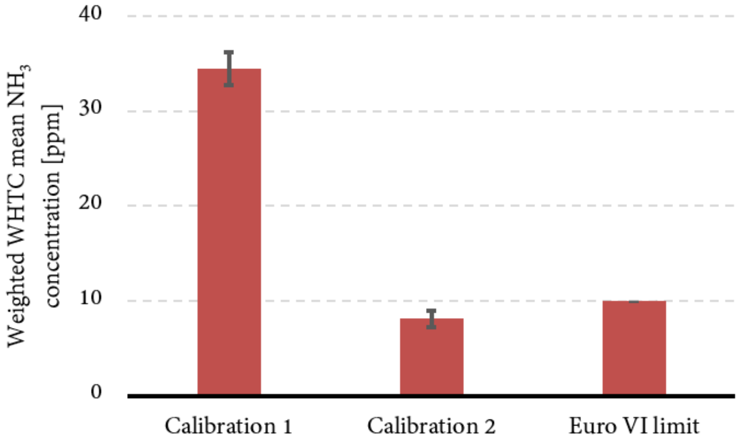

Figure 73. Legislative (mean, weighted) NH_3 concentrations for the two calibrations tested, with the applicable Euro VI NO_x limit

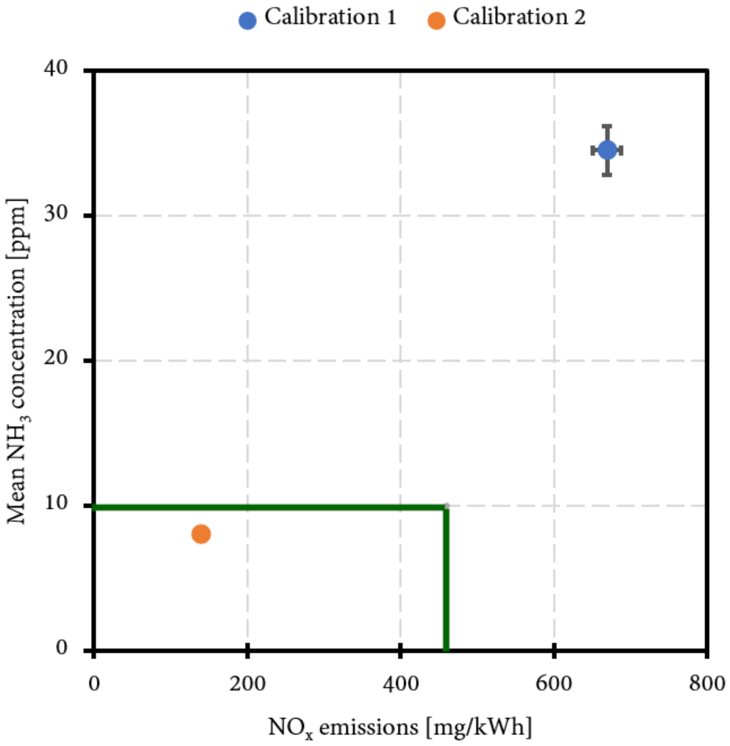

Figure 74. Legislative results (work specific gravimetric NO_x and mean NH_3 concentration) from the two ECU calibrations tested over the WHTC procedure (cold and hot tests, with legislative weighting)

Note that in Figure 74 the error bars are smaller than the datapoint itself in the case of Calibration 2. The area bounded by the dark green line shows the Euro VI limits (460 mg/kWh and 10 ppm). As summarised in Figure 72, use of one calibration lead to much greater values for emission of NO_x and increased mean concentration of NH_3 than the other calibration – the differences being a factor of approximately 4.8 and 4.3, respectively. Thus, from the point of view of NO_x and NH_3 emissions, one ECU calibration caused significantly worse environmental performance, with emissions which exceeded the Euro VI limits for both compounds. However, the fact that both NO_x and NH_3 were higher in one case than in the other would appear to contradict the much-referenced and oft-mentioned trade-off relationship between tailpipe emissions of those species. Elevated (and diminished) concentrations of NO_x and NH_3 occur at different points in the test sequence, characterised by highly variable exhaust mass flow rates. Notwithstanding the positive correlation between the final NO_x and NH_3 results shown above, instantaneous concentrations of the two species were strongly inversely correlated, with a classic trade-off type relationship (Pareto front) in evidence, as shown in Figure 75.

The observation that the majority of the datapoints are so close to the axes (especially in the case of calibration 2) strongly supports the of-mentioned hypothesis that the instantaneous redox conditions (for which λ is a good proxy) cannot support substantial post-TWC emissions of NO_x and NH_3 simultaneously. In order to further examine this point, the data obtained from the hot WHTC performed using calibration 2 were taken for further analysis.

Figure 76 and Figure 77 show the relationship in further detail.

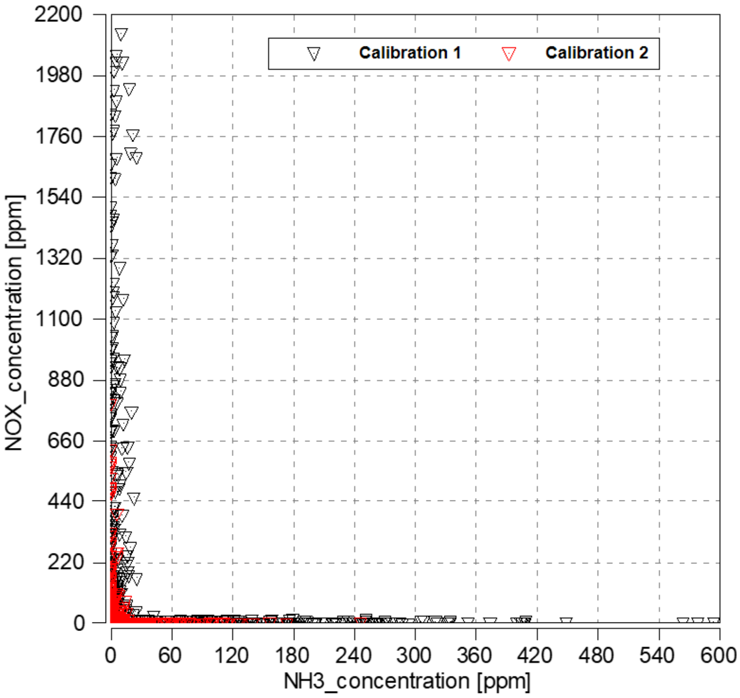

Figure 75. Instantaneous time-shifted concentrations of NH_3 and NO_x during the WHTC hot test, for both calibrations tested

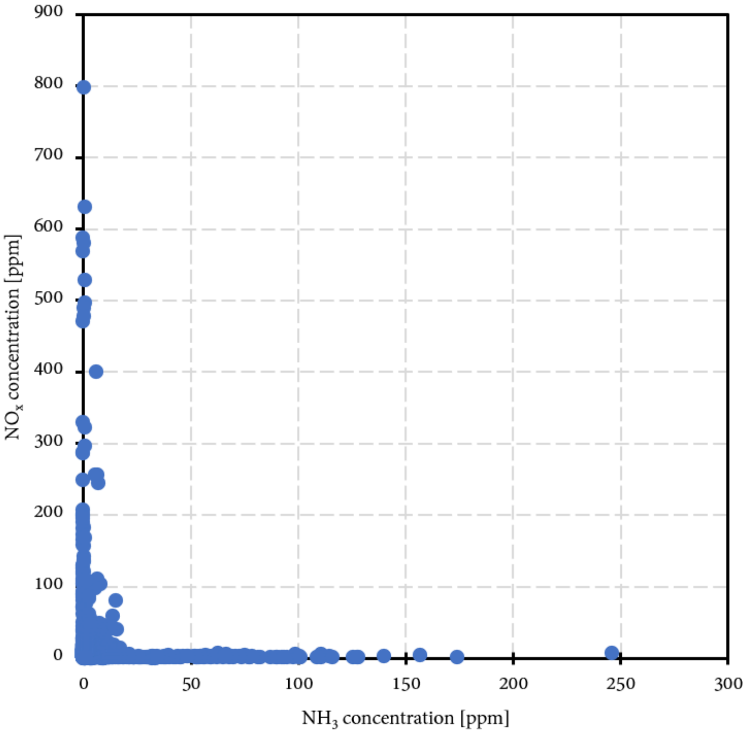

Figure 76. NO_x and NH_3 concentrations occurring during the WHTC hot test on calibration 2

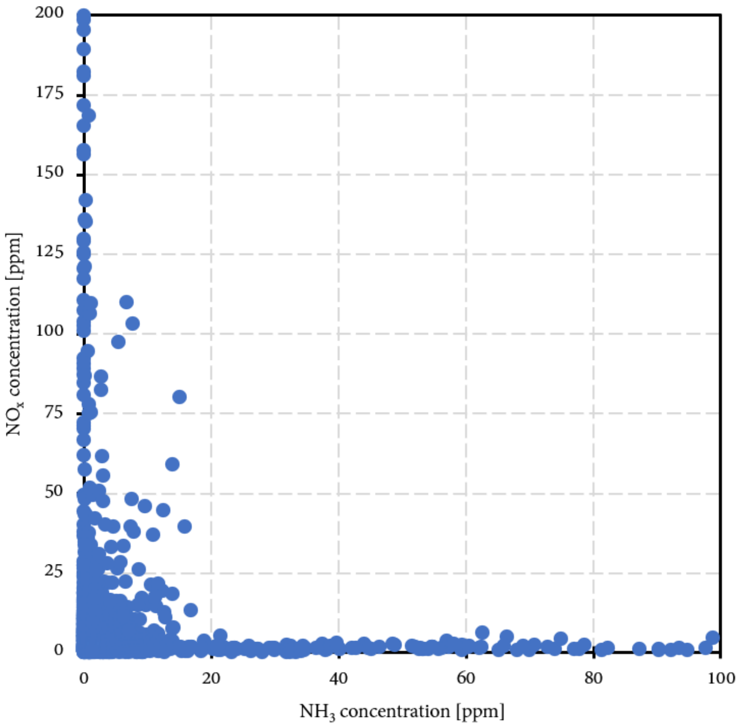

Figure 77. NO$_x$ and NH$_3$ concentrations (NO$_x$ < 200 ppm; NH$_3$ < 100 ppm) occurring during the WHTC hot test on calibration 2

As the figures show, the trade-off type relationship is strong. Note that fact that the figures present data from the hot WHTC, for which the temperature of the aftertreatment system is high (well in excess of NO T50). Nevertheless, a relatively large proportion (some 45%)[20] of datapoints do not lie on either of the axes, i.e. did not represent a situation where the presence of detectable concentrations of NOx and NH$_3$ were mutually exclusive. Note, however, that the accuracy of the measurement (especially for lower concentrations and especially in the case of NH$_3$) and time alignment of concentration traces are potentially complicating factors which must be recalled in this context.

The EU NH$_3$ concentration limit (mean) of 10 ppm was found to correspond to the 89th percentile of all measured NH$_3$ concentrations. The corresponding 89th percentile of NO$_x$ concentration values was found to take a value of 17.1 ppm. These two values were taken as reference levels and added to the plot, as shown in Figure 78. In this manner, the origin can be moved to a new point defined as the intersection of the two reference levels and thus the dataset can be divided into 4 sectors {1,2,3,4}, as shown in the figure.

The proportions of datapoints within sectors 1, 2, 3 and 4 (as shown in Figure 78) are given in Table 13. Note the fact that the proportion of datapoints for which both concentrations of both species were below the reference levels was almost 80%, as well as the extremely low number of datapoints in sector 1.

Table 13. Breakdown of datapoints by sector (refer to Figure 78)

Sector	Proportion of datapoints [%]
1	0.5
2	10.4
3	78.7
4	10.4

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[20] For this calculation the accuracy of the analyser is of paramount importance. For the indicative calculation given here, all concentrations of either species taking values <2 ppm are treated as lying on the axis (or axes).

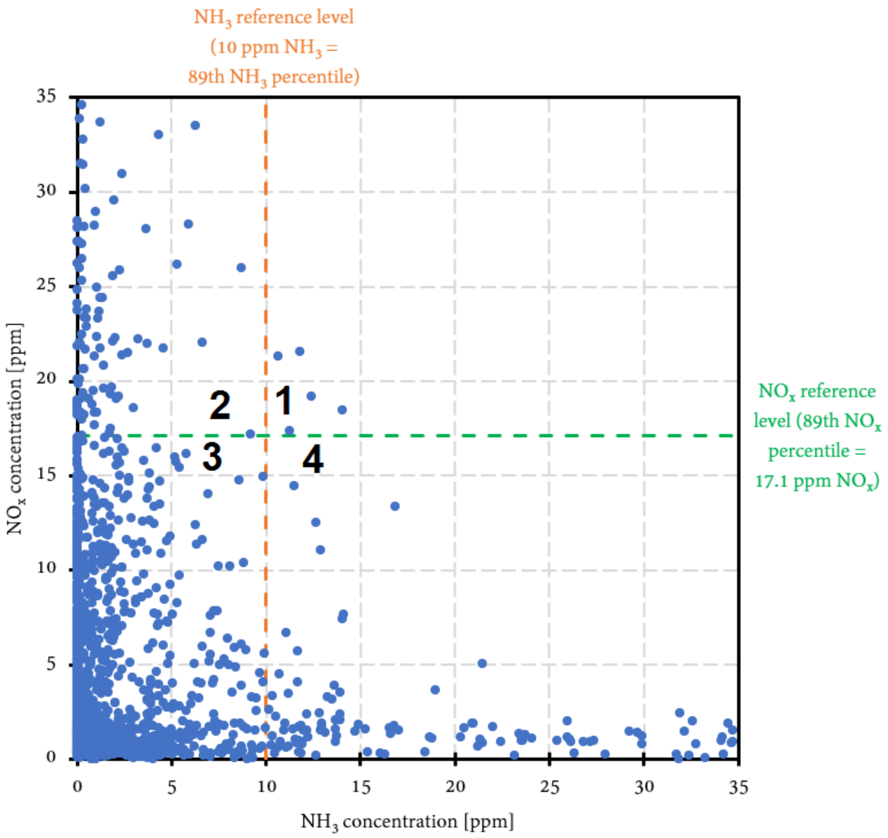

Figure 78. NO$_x$ and NH$_3$ concentrations (both excluding values >35 ppm, for clarity from the graphical point of view) occurring during the WHTC hot test on calibration 2, with dashed lines representing the suggested reference levels (refer to the text)

Thus, the majority of the datapoints occurred in the area where concentrations of both species were relatively moderate, which corresponds to the overall emissions level as quantified by the legislative metrics (Figure 74).

In this specific engine dynamometer measurement setup, where the post-TWC exhaust gas sample is taken very close to the TWC outlet, the surface area of metallic exhaust line components available for adsorption and condensation of liquid water is significantly lower than in the case of a typical passenger car. The WHTC hot test commences under conditions where the temperature of the exhaust line is high, thereby creating unfavourable conditions for the temporary storage of NH$_3$ (high substrate temperature, low likelihood of condensation, even where the fuel type is CNG). The practical implication of the very limited extent of this effect is that the clear trade-off relationship is essentially unconfounded by NH$_3$ storage and release effects, including those caused by liquid water. However, over the entire test procedure, when processing the results as required by the legislative test method, the clear relationship shown in Figure 47 was not visible (as discussed above). The general tendency for calibration 2 to be characterised by lower instantaneous concentrations of both species (i.e. the majority of datapoints were closer to the origin) is in agreement with the final legislative results (Figure 46). Thus, examination of instantaneous data allow examination of the NO$_x$/NH$_3$ emissions balance at a given operating point, but can be of limited utility in terms of predicting legislative compliance. The situation is further complicated by the fact that the NO$_x$ limit applies to a flow-weighted gravimetric value, whereas the mean NH$_3$ concentration gives equal weighting to all measurement points, regardless of the exhaust gas flow rate.

Investigation into long-term TWC ageing on market fuels of variable composition and the resulting impact on NH_3 formation in a HD TWC

Here two aftertreatment systems designed as the main unit for the aforementioned HD CNG engine meeting the Euro VI standard were subjected to accelerated ageing. The two aftertreatment systems were each aged on a single CNG fuel type and were subjected to periodic emissions tests on the engine. Ageing was carried out by running a demanding duty cycle using two different CNG fuels. The entire ageing procedure can be considered broadly equivalent to the Euro VI durability requirements for HD duty vehicles, namely 160000 km. Fuel 1 represented an average case European market CNG fuel, while Fuel 2 represented a fuel type of lower quality, of sulphur content some 3 times higher than that of Fuel 1 (mean values: 8 ppmS and 25 ppmS). No emissions measurements were performed during ageing. For the periodic WHTC emissions tests, reference was used CNG fuel (as required for certification testing according to Euro VI legislation) and regulated emissions were measured both upstream and downstream of the aftertreatment system using an AVL AMA emissions bench and associated automation system. Ammonia was measured from a sampling point immediately downstream of the second TWC of the aftertreatment system, using a dedicated laser diode detector which was calibrated before each test and thoroughly purged following each period of measurement.

For the particular engine tested, for the combined WHTC with legislative weighting of results, a level of $DeNO_x$ effectiveness of approximately 95% is required in order to meet the Euro VI NO_x limit of 460 mg/kWh. Such a level of $DeNO_x$ effectiveness was far exceeded at low ageing stages, but as ageing increased, the $DeNO_x$ effectiveness fell below this level and thus the NO_x limit was exceeded. As engine-out NO_x emissions and indeed the temperature of the exhaust gas were found to be invariable and highly repeatable, tailpipe NO_x is a direct function of $DeNO_x$ effectiveness, which was affected by ageing. For the units under test, the ability of the TWC to convert NO_x with high effectiveness was found not to depend directly on the formation of NH_3; i.e. that the NO_x-NH_3 trade-off was not applicable in this case and at this scale, since ageing of the units under test caused the following overall tendencies, simultaneously:

1. lower $DeNO_x$ efficiency (more so in the case of fuel 2),
2. higher NO_x emissions (more so in the case of fuel 2),
3. variable changes in mean NH_3 concentrations (with no significant, consistent long-term increase observed).

Observations (1) and (2) were as expected; ageing caused increased NO_x emissions, with the rate of increase somewhat greater in the case of the fuel of higher sulphur content (fuel 2). Observation (3) is discussed in the remainder of this section. In Figure 79, NH_3 results obtained according to the EU HD type approval procedure are presented for the two aftertreatment systems tested (each of which was aged on CNG fuel of somewhat different composition). Two full WHTC test runs (i.e. both hot and cold) were performed on each aftertreatment system at each ageing stage.

The Euro VI NH_3 concentration limit of 10 ppm was not exceeded during any test (in terms of the raw cold/hot result, as well as the weighted result) and weighted NH_3 concentrations did not exceed 7.2 ppm (i.e. 72% of the limit). There was a surprising lack of agreement in the mean NH_3 concentration between the two aftertreatment systems at the first ageing stage, but thereafter differences were smaller. As ageing was carried out between the agreement of the mean NH_3 concentrations improved; nevertheless, the behaviour was chaotic and non-monotonic, with results from the second and final ageing stages being at very similar levels. The relatively constant NH_3 levels observed for the majority of the ageing stages provide evidence against the oft-mentioned hypothesis that high $DeNO_x$ efficiency is achieved (at least in part) via significant formation of NH_3, since there was no evident correlation between those parameters, as shown in Figure 80.

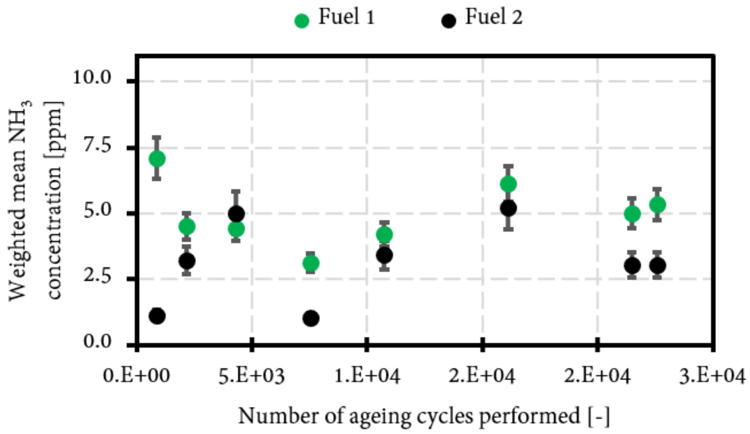

Figure 79. Mean NH_3 concentration measured during the WHTC test procedure (weighted mean of cold and hot results), as a function of the number of ageing cycles performed prior to testing

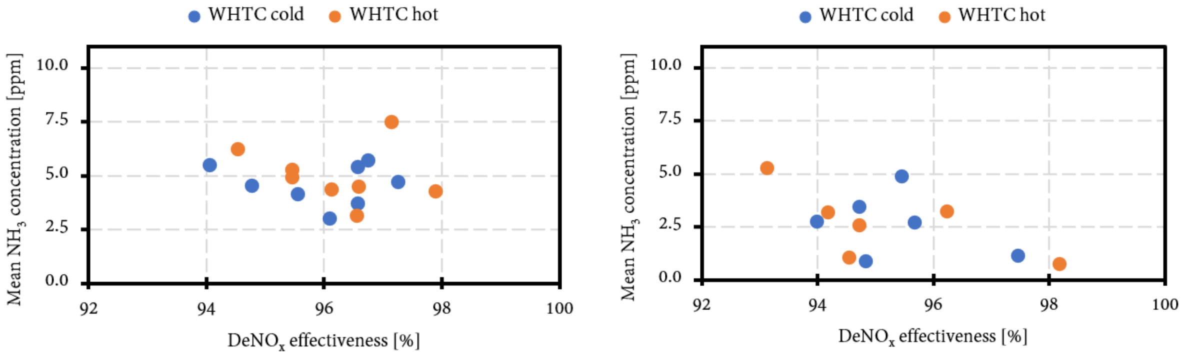

Figure 80.

a) Mean NH_3 concentration as a function of the measured $DeNO_x$ effectiveness for the WHTC cold and hot tests at various ageing stages with the aftertreatment system aged on fuel 1

b) Mean NH_3 concentration as a function of the measured $DeNO_x$ effectiveness for the WHTC cold and hot tests at various ageing stages with the aftertreatment system aged on fuel 2

Nevertheless, the data are supportive of the hypothesis that selectivity towards NH_3 increased somewhat as ageing progressed, since less reduced NO_x was available for participation in NH_3 formation (as more NO_x left the aftertreatment system unreacted), yet the concentration of NH_3 did not fall consistently. The reduced $DeNO_x$ effectiveness of the aftertreatment systems is most probably primarily attributable to reduced OSC, which is also known to influence NH_3 formation, especially over a highly transient and demanding duty cycle such as the WHTC. Notably, Nevalainen et al. [325] reported no real increase in NH_3 formation for a CNG TWC following extended ageing, yet that study reported a significant increase in N_2O formation following such ageing. (N_2O measurements were not available for the experimental work reported in this section.) Despite the substantial difference in the sulphur level of the two fuels, there was a small difference in the mean NH_3 concentration when comparing the two aftertreatment systems at a given ageing stage – however, the difference in mean NH_3 concentration observed at the final ageing stage may possibly be significant. Further characterisation of the impact of long-term ageing equivalent to full useful life on the $DeNO_x$ efficiency and RNC selectivity is recommended; additional dimensions of such research could consist of evaluations of the impact of parameters including Pd and Rh content, as well as OSC characteristics, on RNC emissions throughout the aftertreatment system's full useful life. The potential introduction of concurrent gravimetric (rather than mean concentration-based) NH_3 and N_2O limits in the Euro VII standard provides compelling motivation for such investigations.

For each of the two aftertreatment systems used for testing, $DeNO_x$ effectiveness over the cold and hot WHTC tests at a given ageing stage were observed to be moderately correlated ($R^2 \approx 0.8$). A basic empirical observation was that the ratio of the mean NH_3 concentration values for the hot and cold WHTC tests was relatively consistent, taking values of approximately 1.12:1 (hot:cold), thus arguing against a strong cold start effect during the WHTC for this particular powertrain. This is deemed likely to be linked to the relatively limited use of enrichment at cold start for CNG engines (at least in comparison to petrol-fuelled counterparts), and perhaps to the level of involvement of the CH_4 molecules which dominate CNG fuel in the TWC-promoted NH_3-forming reactions at the temperatures which predominate during powertrain warmup.

6. Conclusions and Summary

6.1. Overall conclusions

This thesis has presented a detailed literature review and a body of experimental work on the topic of exhaust emissions of NH_3 from vehicles with SI engines. The literature review showed that the topic is relatively uncontroversial – no published study was identified which reported no measurable NH_3 emissions from vehicles with such powertrains. However, the literature review also revealed great variability in the emissions factors reported even for vehicles of similar age, tested using the same test procedure. Two key general tendencies identified in the literature were the importance of the test procedure, particularly with regards to transient operation and also the strong dependence on exhaust gas composition (primarily quantifiable in terms of λ) and TWC temperature. A further tendency which appears in the literature, albeit much more so in the case of more recent studies, is that of cold start emissions. Indeed, the majority of the literature from recent years reports that NH_3 emissions are dominated by cold start. The concept of system nitrogen partitioning and selectivity was discussed in light of the most significant findings from the literature review; the behaviours of PGMs, support/OSC materials and combinations thereof were and analysed. It was identified that Rh generally has a lower propensity to facilitate formation of NH_3, compared to Pt and Pd and that Rh's behaviour is little modified by the support material. The results of the experimental work presented here confirmed the literature consensus that emissions from modern vehicles are, in many cases, much higher following cold start and that a relatively wide range of vehicle operation conditions do not lead to the emission of significant quantities of NH_3. However, even where gravimetric NH_3 emissions are at low levels, it remains the case that NH_3 is the dominant RNC present in the exhaust gas under a wide range of vehicle operating conditions. The only available reference level, the mean concentration-based limit of 10 ppm, was found to be exceeded in the vast majority of cases, with only a limited sub-set of vehicles with certain powertrain characteristics showing mean NH_3 concentrations below this level. Significantly, the vehicles with full hybrid powertrains showed low distance-specific emissions of NH_3. Testing performed on an HD engine showed examined the relationship with NO_x for a given engine calibration and confirmed the complexity of the trade-off effects between those species.

6.2. Detailed conclusions

The literature review presented in this thesis releveled that certain aspects often have limited or modest impacts on NH_3 emissions, or at least lead to changes smaller in magnitude than those caused by other factors. Parameters in this category include ambient temperature and fuel composition. The case of ambient temperature is complex, since low ambient temperatures lead to significantly more fuel-rich air:fuel ratios being used following cold start, thereby making the direct impact more a case of sensitivity to λ than to temperature itself (as is also the case for exhaust emissions of CO). A further complicating factor relates to interactions between NH_3 and condensed water in the exhaust line; under certain scenarios, increased NH_3 production within the TWC could fail to translate into increased quantification of NH_3 in the exhaust gas exiting the tailpipe. Data for certain comparisons are present in the literature, but in many cases the number of studies available for consideration (and the number of vehicles involved in each study) was relatively low. Examination of the reported propensity for NH_3 formation from the literature revealed the following overall consensus: Pt>Pd>Rh, although it was found that the support type and the OSC were also key determinants of NH_3 formation tendencies for Pt and Pd, but not Rh. OSC was identified as a very strong determinant of tailpipe NH_3 emissions and variable ageing-related degradation of OSC was identified as a likely primary cause of strong differences in the magnitude of NH_3 emissions between similar vehicles, especially considering the possibility of divergent vehicles mileages.

The experimental work allowed multiple key conclusions to be drawn, which may be summarised as follows:

- Cold start was identified and confirmed as a major contributor to NH_3 emissions from modern vehicles. Indeed, some vehicles' NH_3 emissions profile are dominated by the cold start event, at least over widely used driving cycle like the WLTC.
- Demanding driving cycles were identified and confirmed as causing greater formation of NH_3. However, in the case of broadly comparable driving cycles, this does not always translate into increased distance-specific emissions, due to the impact of the distance covered by the driving cycle.
- Certain vehicles (including hybrids) show low NH_3 envisions under a wide range of driving conditions and have overall NH_3 emissions on the order of a few mg/km. The frequent engine restart event experienced by vehicles with hybrid powertrains hybrids lead to the formation of NH_3, but this appears to be more than compensated for by the periods during which the ICE is not being fuelled and probably also by the availability of electric torque to meet power demand, thereby limiting the use of enrichment during accelerations (at least somewhat).
- Certain vehicles are high-emitters, showing elevated NH_3 concentrations in their exhaust gas under a very wide range of powertrain operating conditions, even when thermally stabilised and even at idle. The reason for this is not fully clear, but may relate more to the characteristics of the TWCs fitted to such vehicles (in their field-aged states) than to any property of the engine itself or the powertrain control strategy.
- Fuel cut-off conditions cause an immediate strong decrease in the measured concentrations of NH_3 (and thus in gravimetric NH_3 emissions); such events are typically accompanied by measurable NO_x breakthrough, meaning that the instantaneous value of $\{NH_3\}$ falls until such time as NH_3 production recommences. This observation is in line with the literature consensus, particularly the point that higher levels of oxygen strongly supresses TWC-facilitated NH_3 formation reactions and also favour NO_x breakthrough.
- The specifics of the speed trace (and especially the demanded wheel work) around the time of TWC light off (specifically NO T50) appear to have a significant impact on NH_3 emissions behaviour and can noticeably increase emissions. In this context, the so-called "crescendo" effect is to be of high relevance.
- Very low load driving cycles can lead to reduced NH_3 emissions, which is in line with other conclusions regarding the impact of λ, fuel flow rate, etc., but there is evidence of a "flushing" effect, whereby previously formed NH_3 remains within the exhaust line (and also in solution within condensed water) for a period of time, being released when the power output of the engine increases. This "latent NH_3" could be a noteworthy complicating factor for full hybrid vehicles.
- For instantaneous observations, or consideration of relatively brief periods, such as an acceleration event, RNC emissions are dominated either by NH_3 or by NO_x (which consists almost entirely of NO). The RNC flux is normally dominated by N_2O only once during any normal driving cycle, within a narrow temperature range below the range corresponding to T50 TWC.
- Notwithstanding the previous point, results from entire test procedures do not necessarily show this trade-off type behaviour; the form of the relationship between the total quantity of NH_3 emitted and the total quantity of NO_x emitted can take positive values.
- Aftertreatment system ageing leads to increased NO_x emissions via a reduction in $DeNO_x$ effectiveness, but the resulting impact on NH_3 emissions is complex. The work presented here shows no real evidence of a conclusive link between ageing and NH_3 emissions. Similarly, for vehicle testing, no correlation between NH_3 emissions and test vehicle mileage was observed, despite frequent mention of such a correlation in the literature.

- Overall, the vehicles tested in this work showed relatively typical distance-specific NH_3 emissions in comparison to other studies from the past decade, as summarised graphically in Figure 81. However, direct comparisons are complicated by multiple aspects such as test procedure, driving cycle, vehicle mileage, etc, as well as the increasingly relevant topic of highly electrified powertrains. This study has confirmed that many modern vehicles have NH_3 emissions on the order of ~20 mg/km.

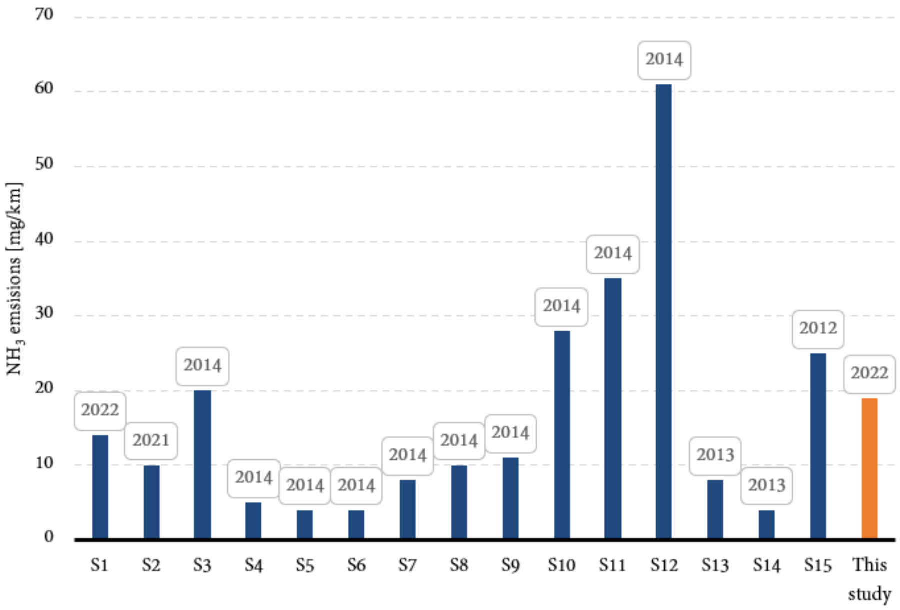

Figure 81. Graphical comparison of distance-specific NH_3 emissions factors from various studies cited previously in this thesis published within the years 2012-2022. Labels give the year of publication of the study. Efforts have been made to exclude results obtained from vehicles with hybrid powertrains and testing conducted at low ambient temperatures

6.3. Methodological conclusions

The experimental work conducted in this study was carried out mindful of the issues associated with NH_3 measurement in the automotive context reported in the literature. It was shown that analyser purging with ambient air and frequent changes of the pre-filter were generally sufficient to obtain NH_3 emissions results of acceptable quality. The study of NH_3 emissions resulting from driving cycles commencing with very low load underlined the relatively high dependence of overall NH_3 emissions factors on the initial periods of engine operation, during and after TWC NO T50 is reached. This fact is significant, since the combustion engines of hybrid powertrains often experience low load during the initial portions of test procedures. It was shown that the so-called light-off NH_3 surge can be significantly delayed at low load operation, causing a breakdown of the empirical relationship between NH_3 emissions and parameters such as NO breakthrough and λ. For very short driving cycles, this might lead to considerable underestimation of NH_3 emissions, since extending the sampling period slightly could cause release of such latent NH_3, as observed in the experimental work reported here. Such effects are of much greater relevance for vehicles with hybrid powertrains, especially plug in hybrids, where the relationship between demand for wheel power and internal combustion engine operating parameters is highly complex (and often weak). In this context, the use of a single driving cycle (such as the WLTC) for demonstration of NH_3 emissions control is perhaps inadvisable, especially in the case of hybrids, since even small alterations to the specifics of the speed trace can be expected to noticeably alter the NH_3 emissions behaviour. Indeed, counteracting effects (including complex thermal effects) and the impact of cycle distance can sometimes cause the unexpected result of distance-specific NH_3 emissions being higher for less demanding driving cycles [321].

The RNC concentration coefficient concept – given the notation {RNC} in this work – proved to be a useful tool for time-resolved analysis of NH_3 (and RNC emissions in general), and underlined the fact that under a wide range of powertrain operating conditions, the molar RNC flux is dominated by NH_3, with values sometimes approaching a value of 1.0. During cold start driving cycles of normal length, such as the WLTC, NEDC and FTP-75, the values taken by $\{NH_3\}$ during the entire test procedure are significantly lower than 1, but still high for many vehicles, lying within the approximate range 0.7-0.8 (refer to Figure 30). Nevertheless, the value taken by $\{NH_3\}$ bears little relation to the final distance-specific NH_3 emissions measured during that test and the concept is of insufficient explanatory power to accurately predict NH_3 emissions.

A very large number of exhaust emissions studies are available which do not include measurements of NH_3. This situation is slowly changing, as reflected by increasing numbers of publications which report and discuss NH_3 emissions. However, even where NH_3 is not measured directly, or where NH_3 + NOx sum is the only RNC measurement available, signals can be made use of to examine NH_3 emissions behaviour [284] – where it is known that the value of $\lambda \leq 1$, it can be assumed that in the vast majority of cases the signal generated by the sensor corresponds to NH_3 (and not NO_x), and vice-versa (see also [183]). A methodology put forward by the EPA based on four key parameters (NO_x, lambda, exhaust temperature and vehicle acceleration) [326] would appear to be eminently suitable for modelling NH_3 emissions (or at least NH_3 concentrations). While such an approach is eminently unsuitable for legislative testing (demonstration of compliance with type-approval requirements), it could prove a cost-effective method for automotive industry R&D and indeed for monitoring and surveillance purposes.

6.4. Utilitarian conclusions

The low NH_3 emissions demonstrated by vehicles with hybrid powertrains, as well as the relatively modest NH_3 emissions measured from Euro 5 and Euro 6 vehicles are indicative of a reduction of the scale NH_3 emissions in relation to levels reported in the literature in recent years. This apparent change has occurred despite the lack of any rigorous legislative requirement for NH_3 emissions. However, it must be recalled that more recent model year vehicles have lower mileages and results presented here represent Nevertheless, as revealed by the examination of the literature, NH_3 emissions are sensitive to TWC parameters such as PGM loading, individual PGMs, the OSC and its availability as a function of temperature and even the support material and its interaction with exhaust gas components, tendency to promote WGS and SR, etc.

The fact that certain vehicles with non-negligible mileages have moderate – or even very low – emissions of NH_3 proves that it is arguably realistic to introduce a gravimetric NH_3 emissions limit with a low numerical value. Hybrid powertrains and vehicles with larger-displacement ICEs with very high power:mass ratios were identified as being characterised by overall lower NH_3 emissions. Other vehicles with less exceptional powertrains showed low emissions, which may have been related to the specifics of their TWCs. Conversely, unexpectedly high emissions were also observed for some vehicles, even under very undemanding driving conditions and even excluding cold start effects, with no single, underlying identifiable cause. This observation points to the need for continued research in this area, particularly in terms of identifying high-emitters and drawing appropriate conclusions regarding how NH_3 emissions from new vehicles (and even from in-use vehicles) might perhaps be reduced. In this respect, data generated by remote sensing campaigns are of high utility.

6.5. Perspective conclusions

6.5.1. General remarks on perspectives for legislative control of NH_3 emissions from road vehicles

As the first known quantitative assessment of NH_3 in vehicle exhaust gas dates to 1967 and the first known mention of catalytically-induced formation of NH_3 in the automotive context in the literature comes from 1972, the length of time for which the issue of ammonia emissions from vehicles has been known, without an effective gravimetric NH_3 emissions limit being mandated in any jurisdiction, is now some fifty years. During that time, the topic has generally remained a low profile, despite relatively frequent mentions in the technical literature, especially from around the year 2000 onwards.

Notwithstanding the considerable attention given to nitrogen speciation and ammonia formation in the applied catalysis experiments of the 1970s, for decades, even laboratories designed for R&D on engines, vehicles and aftertreatment systems typically did not feature NH_3 measurement. In recent years, the roll-out of Diesel-SCR systems (including for passenger cars) has increased the profile of NH3 measurement and caused many laboratories to invest in NH3 analysers. However, the fact remains that R&D procedures are largely guided by (and essentially based upon) legislative requirements and the probability that NH3 from SI powertrains will be subject to rigorous measurement by default will remain low as long as NH3 is an unregulated pollutant.

As Schuermann et al. [107] pointed out in 1990:

> *"For more than ten years, US legislation has been calling for constant proof from vehicle manufacturers that the exhaust gas treatment systems, which are built into vehicles to reduce the legally controlled emissions, do not release other (unregulated) components in such concentrations as to represent an unjustifiably high health risk".*

Schuermann et al.'s brief assessment of the results was that exhaust emissions of NH_3 were not a major contributor to observed ambient levels of NH_3, echoing a similar finding from some seven years prior [327]. However, the threshold of any pollutant deemed to constitute an unjustifiably high health risk is likely to have changed since the late 1980s. Indeed, in the era where regulated emissions were subject to the contemporary legal limits but nevertheless very high by modern standards (e.g. NO_x up to ~1000 mg/km), emissions of unregulated species such as NH_3 may not have appeared worthy of attention in terms of their impact – but the dramatic reductions which have been achieved for regulated pollutants (including NO_x) mean that other, unregulated compounds increase in relevance, even in cases where their emissions level remains unchanged. US law contained a clear reference to unregulated pollutants and the possibility of formation thereof in aftertreatment systems, which were to be urgently investigated in the early 1990s and used in determining future emissions requirements for road vehicles [328]. The precise reasons why NH_3 was never added to the list of regulated pollutants in the US are not apparent in the technical literature; in the case of Europe and various Asian markets, the precedent set by the US authorities is most likely the main reason. In 2007, during the process of setting Euro 5/6 emissions limits the European Commission stated [329]:

> *"The Commission should keep under review emissions which are as yet unregulated and which arise as a consequence of the wider use of new fuel formulations, engine technologies and emission control systems and, where necessary, submit a proposal to the European*

> *Parliament and to the Council with a view to regulating such emissions".*

Yet the intention expressed above has self-evidently not translated into concrete action in the case of NH_3 (with the partial exception of HD powertrains, where it was spurred by the adoption of SCR and expanded to spark-ignition engines on the general principle of fuel-neutral limits). Furthermore, following decades of reliance on the CVS-bag method (i.e. batch quantification of diluted emissions) for demonstration of legislative compliance under laboratory conditions, there is considerable reluctance to mandate an emissions quantification method requiring the measurement of raw (undiluted) exhaust, for a variety of reasons, the requirement for a real-time exhaust volumetric flow vector being the most prominent.

6.5.2.Future regulation of exhaust emissions of NH_3 from road vehicles with SI engines

At the time of writing, multiple jurisdictions are taking active steps to devise and implement more stringent exhaust emissions standards for road vehicles. In the EU, this takes the form of the planned Euro 7 (LD) and Euro VII (HD) standards, which are expected to be unveiled in the first half of 2022. A significant body of opinion states that the planned standard will deviate from previous standards in three key areas:

1. increasing focus on real-world emissions, i.e. on demonstration of emissions compliance outside the laboratory, under real conditions of use, with emissions measured by PEMS;
2. the introduction of additional (new) limits for compounds which are currently unregulated and many of which have traditionally been viewed as being of low importance in the automotive context;
3. the adoption of a fuel- and technology-neutral approach, whereby limits for a given vehicle category take a single value, regardless of vehicle fuel type or powertrain specifics such as injection system type.

Significantly, the aspect mentioned in point 2 (the introduction of new limits subjecting new chemical species to test procedures and legislative limits) is expected to apply in the case of ammonia. While the Euro 7/VII standards remain unconfirmed at the time of writing, it has been stated that the expected limit values are 10 mg/km (Euro 7) [83] and 65–70 mg/kWh (Euro VII) [330]. Certain previous documentation serving as input for the draft proposals mentioned significantly more stringent limits for both LD and HD, namely 5 mg/km and 40 mg/kWh, respectively. Somewhat less stringent limits have been put forward in recent proposals concerning Euro 7/VII [331].

As long as NH_3 remains excluded from the light-duty type approval procedure, the probability of it being monitored during periodical technical inspections (PTI) is essentially zero. However, regulation of a species during the type approval procedure is not an automatic mandate for measurement/assessment of that species during PTI. As an example, the topic of monitoring NO_x emissions during PTI is the subject of a long-running debate within the EU which has not yet been resolved [332]. Note, however, that China has a PTI procedure for vehicles with SI engines which includes measurement of NO_x emissions, albeit with a lax limit of 0.7 or 1.3 g/km [333].

In any case, as is also the case for certain other pollutants and aftertreatment system types [334], [335], measuring concentrations at idle would not prove sufficient, since comprehensive NH_3 screening would require engine operation under two conditions which are not reached during thermally stabilised idle:

- exposure to high load conditions, necessitating the imposition of rotating resistance on the drive wheels (whether 2 or 4), as well as simulation of inertial effects;

- operation following cold start (during normal driving, or indeed at idle).

An interesting precedent has been set here by the Chinese government, which has introduced a driving-based test procedure for verification of exhaust emissions during technical inspections [336]. Furthermore, the aforementioned procedure includes a gravimetric limit for NO_x emissions (albeit at a highly lenient level). While the procedure given in [336] does not require monitoring of NH_3 emissions, and while the low speed, constant-speed test procedure creates conditions unconducive to high formation of NH_3 (no cold start; no high load), the concept of performing verifications of exhaust emissions under non-idle driving conditions is a foundation which could be built upon in the future.

Empirically-derived correlations of vehicle age (and emissions standard) with emissions (of any type, including NH_3) are invariably confounded by factors such as powertrain design trends, evolving vehicle weight, etc. In any case, in multiple peer-reviewed studies, authors have urged the adoption of an NH_3 emissions limit for road vehicles, with the general assumption being that the limit would be fully technology- and fuel-neutral. Preparatory discussions for the next round of EU automotive emissions legislation [337] have also included the topic of so-called additional pollutants, of which NH_3 is arguably the most prominent (at least at the time of writing).

Given the multifaceted relationships between NO_x and NH_3 and the fact that NO, NO_2 and NH_3 exist on a redox continuum, any discussion of an NH_3 limit must by necessity be linked to NO_x emissions limits (current and/or future). A further layer of complexity may be introduced at this point, namely that for some time pressure has been growing to consider the introduction of a limit for exhaust emissions of NO_2. As the density used for the conversion of concentration to mass gravimetric calculation in the case of NO_x emissions is in fact the density of NO_2, density is not a variable and thus any NO_2 limit would in fact be directly relatable to – and controlled by – the concentration of that species (i.e. molar ratio of NO:NO_2) in the exhaust gas. As NH_3 is not produced by the combustion reaction (unlike NO_x), it would be reasonable to require that exhaust emissions of NH_3 be lower than exhaust emissions of NO_x. Here the question of the basis for quantification of "emissions" arises again, since gravimetric emissions calculations involve the use of the density of the compound in question. However, a given concentration of NH_3 or NO_x translates into significantly different gravimetric emissions results. Ammonia is a single compound with an agreed density of 0.76 g/dm3 under standard conditions, while NO and NO_2 self-evidently have different densities and the use of the density of NO_2 as the legislative density of NO_x represents a "worst-case" assumption (i.e. where only NO_2 is present and thus the NO:NO2 ratio is 0). As the deleterious impacts of a gaseous pollutant can be related much more strongly to the number of molecules emitted (rather than the total mass of those molecules), the large disparity in the density of NH_3 and the density of NO_x would appear to call for some consideration of the density when deriving a gravimetric emissions limit. Following this logic, modifying the current Euro 6 LD SI NO_x limit by the ratio of the molar densities gives the following relation and the following result:

$$60\ \left[\frac{\mathrm{mgNO_x}}{\mathrm{km}}\right] \times \frac{0.76\ [\frac{\mathrm{g}}{\mathrm{dm^3}}]}{2.05\ [\frac{\mathrm{g}}{\mathrm{dm^3}}]} = 22.24\ \left[\frac{\mathrm{mgNH_3}}{\mathrm{km}}\right] \quad (13).$$

Thus, a gravimetric NH_3 emissions limit for LD vehicles with SI engines within the range 20-25 mg/km might be proposed as a reasonable requirement for vehicles required to meet a NO_x emissions limit of 60 mg/km. It is clear that such a limit would not be particularly onerous in many cases, as many vehicles currently on the market have emissions lower than this level – refer to Figure 29. Ensuring that the elimination of NO_x from the combustion reaction does not result in the release of quantities of NH_3 greater than the NO_x eliminated by the system (on a molecular basis) is an approach which would require that NH_3 emissions limits be revised in response to future changes in NO_x limits. However, the current trend in the EU is to move towards fuel-neutral emissions limits [338] (as already exist in the USA).

Therefore, any such requirement should also apply to vehicles with CI powertrains. Following the same logic and applying the same molar density coefficient of 0.76/2.05 to the HD NO_x limit, a figure of 170 $mgNH_3/kWh$ for the WHTC is derived. Similarly, any future reduction in the work-specific HD NO_x limit would require a corresponding reduction in the derived NH_3 limit (as given by (13)).

Emissions associated with cold start, warmup and aftertreatment system light-off are problematic from a wide range of viewpoints and in the cases of a wide range of pollutants. The majority of journeys commence from a cold start and the annual number of cold starts experienced by a passenger car can be high: often on the order of ~500-700, although this figure is naturally subject to massive variation. For short trips, the journey may be terminated well before thermal stabilisation has been achieved, thus leading to very high distance specific emissions of certain pollutants. Such effects can also apply to NH_3 and the fact that the work reported in this study showed fleet-level NH_3 distance-specific emissions factors are higher under cold start urban driving conditions than any other driving condition occurring in the WLTC is of great importance as regards NH_3 budgets and urban air quality. Future efforts to target NH_3 emissions should take this behaviour into account, i.e. by not setting a limit applicable only to a test cycle which covers a high number of kilometres and includes many periods of driving which lead to low NH_3 emissions.

Powertrain evolution has important implications for NH_3 emissions. SI engine control strategies invariably include enrichment (although the frequency and degree to which it occurs varies widely), yet it is clear that most advanced emissions control strategies are moving in the direction at least nominally $\lambda 1$ (so-called “flat”) powertrain calibration maps in the near future [278], [339], [340], [341], [342]. Furthermore, it has been argued that can also apply in the case of engines of very high power density [290]. It should be recalled that even setting aside the topic of exhaust emissions limits (for any species), the use of air fuel ratios rich than stoichiometry ($\lambda < 1$) represents additional fuel consumption and thus reduced energy efficiency and – *ceteris paribus* – increased running costs. Hybrid control strategies typically focus on fuel consumption (e.g. [343]), with minimum attention paid to harmful/regulated/unregulated exhaust emissions [344], yet in fact this trend could help to keep NH_3 emissions low, since fuel thrifting is fundamentally incompatible with enrichment (regardless of the aim of said enrichment). More generally, care must be taken to examine the impact of repeated ICE start-up events on emissions of all types [345], especially where the intervening period of engine operation has been short and of low mean power, meaning that the temperature of the TWC(s) may be low [324]. Such considerations of eminent significance, given the fact that elevated NH_3 emissions are most often correlated with aftertreatment system temperatures in the region of the NO T50 temperature.

Establishment of a gravimetric NH_3 emissions limit would ensure that NH_3 emissions are measured and taken into consideration during the powertrain design, calibration and optimisation process, as well as in base research on aftertreatment systems of all types. A strong incentive would be created to monitor selectivity for NH_3 formation within TWCs under a range of driving conditions and over a wide mileage range. The high variability in LD SI powertrain NH_3 emissions, as well as the fact that certain vehicle models show higher emissions than other similar models, and the fact that deterioration with mileage is modest, implies that there is considerable scope for technical optimisation to reduce NH_3 emissions – crucially, not at the cost of causing notable increases in other emissions such as NO_x or N_2O. In all such efforts – especially those focusing on lowering the NO light-off and general system performance at temperatures in the region of NO T50 – emphatically must include full consideration of the chemical fate of NO molecules converted by the system, attempting to obtain as high a selectivity towards N_2 as possible (i.e. minimising the formation of NH_3 – and indeed N_2O). The only practicable means to force such efforts would be the implementation of an NH_3 emissions limit, ideally accompanied by an N_2O limit (which, as previously noted, already exists in the USA and China).

6.6. Summary

This thesis has followed the topic of NH_3 emissions from TWC-equipped SI engines used in road transport from the first mentions in the literature in the early 1970s to the situation at the time of writing. While road vehicles have evolved significantly over the past ~50 years, the ongoing use of the TWC as the key tool for emissions control method has remained ever-constant. While combustion events in general tend to produce measurable quantities of NH_3, SI powertrains and their fuels are not susceptible to the formation of appreciable quantities of NH_3 without the involvement of catalysis and tailpipe NH_3 emissions occur as a result of the presence of the TWC aftertreatment system, specifically the system characteristics which are targeted so as to provide $DeNO_x$ functionality, i.e. the conversion of NO and NO_2 (chiefly the former) to other chemical forms. Thus, a pollution control device (TWC) is in fact creating pollution under certain operating conditions, converting a non-negligible fraction of one form of pollution into another. While NH_3 is a naturally occurring component of the atmosphere of biological importance and global anthropogenic emissions are dominated by agricultural activities, sewage processing, etc, in urban environments with heavy traffic TWC-generated NH_3 is generally significant and warrants closer attention – and ideally legislative limitation.

As has been shown in this study, both in terms of the results of experimental work and in terms of the examination of the literature, all vehicles with SI powertrains featuring TWCs have measurable NH_3 emissions when tested using widely-used emissions test procedures (driving cycles). Differences in the magnitude of NH_3 emissions are significant; in some cases, NH_3 emissions are at very low (and even unquantifiable) levels; in other cases, NH_3 emissions can be broadly comparable with NO_x emissions (including for HD engines running on gaseous fuels [273]). Furthermore, NH_3 emissions can even be at a higher level than NO_x (depending on many factors, not least of which is the basis used for comparison of said emissions – gravimetric or molar). As has been confirmed in multiple studies and shown in earlier sections of this thesis, following TWC light-off, under many driving conditions NH_3 is the dominant RNC species in the exhaust, precisely because the rate of NO conversion is very high and selectivity towards N_2 formation is finite. Events characterised by high emissions of NH_3 can generally be divided into two categories: those associated with TWC light-off (sometimes termed cold start NH_3 emissions) and those associated with high load. There can be cross-over between these two categories – and in certain scenarios they may in fact entirely overlap (i.e. coincide in the time domain), but this is normally not the case for measurements performed over widely-used legislative driving cycles.

As regards TWC characteristics and the potential for reducing NH_3 emissions, the literature presents a near-unanimous consensus on the benefits of Rh in terms of high conversion of NO and lower selectivity towards NH_3 formation, compared to Pd and Pt (see [134] for a recent example), yet for certain technical, practical and economic reasons, Pd remains in much wider use in TWC present in new vehicles (and the in-use fleet). Exhaust gas aftertreatment systems with dedicated units designed to remove NH_3 and electrically heated catalysts might also play a role here. Indeed, regarding electrical heating, if it is possible to preheat TWCs and thus avoid prolonger residence within (or even repeated transition through) a thermal window in which NH_3 formation is substantial, then NH_3 emissions might be reduced to very low levels, especially when applied in conjunction with other strategies. Oxygen is identified as a key inhibitor in NH_3-forming reactions and availability of sufficient OSC during λ excursions is a viable strategy for controlling hot-running NH_3 emissions. As a general point, strategies aiming to limit

NH_3 emissions could prove synergistic with other emissions reduction efforts, perhaps most obviously CO, but also other species, including the non-NH_3 RNCs.

At present, measurement of NH_3 is often omitted in automotive emissions contexts, a fact intimately linked to its legal status (i.e. for the most part unregulated in all market, with a limited exception for some larger vehicles in the EU and South Korea, where the limit is concentration-based and generally undemanding). The tendency for NH_3 formation is strongly controlled by variables which can change on very short timescales (engine operating point – λ, temperature, the supply of NO, H_2 as well as CO), as well as those which change on longer timescales (changes in inherent selectivity resulting from gradual physiochemical changes in the TWC, or the ability of the powertrain to maintain close λ control), in addition to variables which are essentially fixed parameters such as TWC design/specification, the temperature residency for typical duty cycles, and fuel specifications. For a given vehicle at a given mileage stage, the range of NH_3 concentrations and gravimetric emissions is controlled by powertrain operating point, temperature and the chemistry of the TWC, which, when considered holistically and in concert, provide generally satisfactory explanations for the highly divergent emissions factors reported in the literature, which have been reported to include significant differences between manufacturers (*ceteris paribus*) [141].

Crucially, while NH_3 remains partially regulated (only in the case of HD vehicles, via a concentration-based limit of low stringency), it is highly unlikely that vehicle manufacturers will incur costs by making changes to their aftertreatment systems or powertrain calibrations merely to reduce the magnitude of NH_3 emissions. Given the above considerations, the case for the introduction of legislative requirements to achieve emissions control of NH_3 from SI engines used in the road transport sector appears strong.

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