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# Characterisation of ammonia emissions from gasoline and gasoline hybrid passenger cars

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ABSTRACT

Recent evidence suggests $NH_3$ emissions from road vehicles play an important role in the formation of fine particulate matter, especially in urban areas. However, there is little data available for $NH_3$ emitted from road vehicles under real driving conditions, in part due to its lack of regulation in vehicle emission legislation. In this study, we use 210,000 vehicle emission remote sensing measurements to evaluate the complex mix of factors affecting $NH_3$ emissions from gasoline and gasoline hybrid passenger cars. The influence of vehicle model year and manufacturer on $NH_3$ emissions is considered, as well as the effect of vehicle deterioration. It is found that the amount of $NH_3$ emitted increases as vehicle mileage increases. A comparison of cold start and hot exhaust $NH_3$ emissions reveals that on average, cold start emissions are a factor of 1.7 times higher. New $NH_3$ emission factors are developed, in addition to speed-emission curves that are potentially useful for national inventories. A new application of remote sensing data is reported, whereby the proportion of failed $CO_2$ measurements for hybrid vehicles provides unique insight into the real world battery use of both conventional hybrid electric and plug-in hybrid electric vehicles, which is used to refine the $NH_3$ emission factors for these vehicles.

## 1. Introduction

The significance of road vehicle emissions as a source of atmospheric ammonia ($NH_3$) is becoming increasingly recognised. $NH_3$ has considerable impacts on both human health and the environment, through its contribution to the formation of fine particulate matter ($PM_{2.5}$) and the eutrophication and acidification effects on ecosystems. Recent studies have found that many existing national emissions inventories underestimate the contribution of the road transport sector to total $NH_3$ emissions. In the US, $NH_3$ emissions from vehicles are anticipated to be more than twice those of the National Emission Inventory (Sun et al., 2017). A recent UK study estimated that total gasoline passenger car $NH_3$ emissions are underestimated by a factor of approximately 2.6 compared with the UK National Atmospheric Emissions Inventory, and emissions in urban areas are underestimated by a factor of 17 (Farren et al., 2020). The emission factors adopted as the basis for the UK inventory are used for national inventory development in many other European countries and therefore these conclusions are likely applicable across the continent.

$NH_3$ emissions pose a significant threat to urban air quality due to their important role in the formation of secondary particles (Erisman and Schaap, 2004). Although agricultural activity dominates overall emissions of $NH_3$, road vehicles have a disproportionately greater impact on the $NH_3$ budget in urban areas (Sun et al., 2017). Around 40% of the US population live in counties where $NH_3$ emissions from vehicles are higher than from agricultural practices (Fenn et al., 2018). In these typically $NH_3$-limited regions, vehicle $NH_3$ can react readily to form secondary inorganic aerosol, such as ammonium nitrate, leading to increased levels of $PM_{2.5}$ (Liu et al., 2015; Chang et al., 2016). Pan et al. (2016) demonstrated this effective pathway to particle formation through a $^{15}N$ isotope study, which showed that fossil fuel combustion-related activities dominated atmospheric $NH_3$ sources during severe haze episodes in urban Beijing, China. More recently, Wang et al. (2020) provided new evidence to rationalise the formation of new particles in megacity environments; they argue localized supersaturation of $NH_3$ and nitric acid ($HNO_3$) and temperature heterogeneities can occur in many cities, creating conditions under which new clusters can grow rapidly by accumulating ammonium nitrate. Emissions from traffic are a strong local source of $NH_3$ and nitrogen oxides (a precursor to $HNO_3$) and may contribute to the transient inhomogeneous conditions in urban environments that enable this rapid particle growth.

With the exception of the Euro VI standard for heavy duty vehicles

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(European Commission, 2011), there are currently no vehicle emission standards to regulate $NH_3$ worldwide. This is not the case for other important pollutants emitted from road vehicles, such as CO, hydrocarbons and $NO_x$, which have been regulated effectively in many countries over the last few decades. In fact, vehicle emissions of $NH_3$ are largely a byproduct of the technologies introduced to meet increasingly stringent $NO_x$ emissions limits. For example, three way catalysts (TWCs), first introduced for Euro I gasoline vehicles in 1992 (Ntziachristos et al., 2019), operate by simultaneously oxidizing CO and unburnt hydrocarbons to $CO_2$ and water and reducing $NO_x$ to nitrogen gas. $NH_3$ formation can occur on the TWC when the reduction of $NO_x$ does not stop at $N_2$ but continues to $NH_3$. Furthermore, many modern diesel vehicles rely on selective catalytic reduction (SCR) as an after-treatment technology, which aims to minimize $NO_x$ emissions through reaction with $NH_3$ on a catalyst surface. $NH_3$ comes from the injection of urea, which must be carefully managed in order to avoid excessive $NH_3$ emission, commonly termed 'ammonia slip'. A US study by Bishop and Stedman (2015) found $NH_3$ to be the dominant reactive nitrogen compound emitted from many newer vehicles, as a result of the growing efficiency of TWCs to reduce $NO_x$ emissions and the introduction of SCR. Despite this, $NH_3$ emission factors used in many national inventories are derived from a limited number of vehicle measurements, often carried out in the laboratory. In recent years, detailed studies of on-road emissions of $NH_3$ using Portable Emissions Measurement Systems have emerged (Mendoza-Villafuerte et al., 2017; Suarez-Bertoa et al., 2017; Vojtíšek-Lom et al., 2018). However, the studies are limited to a small number of vehicles, due to the cost and time restraints associated with these methods. Remote sensing measurements can help address this issue, as large numbers of on-road measurements can be made in a relatively short period of time, encompassing the wide range of vehicle physical characteristics and driving conditions encountered in the real world.

Another potentially important source of $NH_3$ is exhaust emissions from gasoline hybrid vehicles when the combustion engine is in use. Across Europe, conventional hybrid electric vehicles represented 4% of new registrations in 2019, and plug-in hybrid electric vehicles (PHEVs) accounted for a further 1% of new car sales (EEA, 2020). Both types of hybrid rely on the use of a gasoline engine and an electric motor. PHEV batteries can be charged by an external electric power source, by the internal combustion engine (ICE), or through regenerative braking. Conventional hybrid electric vehicles on the other hand rely on charging by the ICE and regenerative braking only. The UK government has committed to bringing all greenhouse gas emissions to net zero by 2050 and the next steps towards cleaner road transport are presented in the Road to Zero strategy (DfT, 2018a). Whilst this strategy recognises that the environmental performance of hybrids (conventional hybrids, PHEVs and range extenders) depends on their use and zero emission range, these vehicles are identified as some of the cleanest vehicles on the market with the potential to bring significant environmental benefits (DfT, 2018b). The Road to Zero strategy identifies the uptake of hybrid vehicles as a key way to help motorists switch to a different way of powering their vehicles and anticipates their use will lead to significant reductions in greenhouse gas emissions. It is therefore important to develop a robust understanding of the behaviour of these vehicles under real driving conditions, from both an air quality pollutant and greenhouse gas emission perspective.

Unlike conventional hybrid electric vehicles, $NH_3$ emissions from PHEVs depend not only on real driving operation but also on the extent to which the vehicle has been charged. In other words, the on-road emissions from PHEVs depend to an unusually large degree on user behaviour, i.e. how diligent someone is in charging their vehicle, and journey length, rather than the performance of the combustion engine itself. The International Council on Clean Transportation (ICCT) recently investigated the $CO_2$ emissions performance of PHEVs, based on real-world fuel economy data. They found that the average utility factor, a measure of the proportion of vehicle km driven using batteries, is 69% for New European Drive Cycle (NEDC) type approval tests but only 37% for real-world driving (Plötz et al., 2020). The disparity between fuel consumption achieved in type approval tests and under real driving conditions is further evidenced by a Dutch study based on fuel card usage data; it was estimated that for modern PHEVs the proportion of km driven using batteries is 25% on average (van Gijlswijk and Ligterink, 2018). These studies provide estimated utility factor values based on reported fuel economy. In this paper, we explore the possibility of using vehicle emission remote sensing measurements to directly measure the amount of time hybrids spend using batteries under real driving conditions. Not only does this provide insight into anticipated $CO_2$ reductions from hybrid vehicles, it also allows measured emissions of $NH_3$ to be adjusted to account for zero exhaust emissions when using batteries.

In this study, we perform a detailed analysis of comprehensive vehicle emission remote sensing measurements to better understand $NH_3$ emissions from gasoline and gasoline hybrid cars under real driving conditions. Uniquely, the failure rate of the $CO_2$ remote sensing measurements is used to provide new insight into the emissions behaviour of hybrid vehicles. Consideration is given to how the emission of $NH_3$ has changed with vehicle manufacture date, as well as the influence of different vehicle manufacturer mixes across the gasoline and hybrid fleets. Important findings in this work related to the effect of cold starts and vehicle deterioration on $NH_3$ emissions are also discussed. Furthermore, a previously developed method for deriving distance-based (g $km^{-1}$) emission factors from remote sensing measurements (Davison et al., 2020) is used to generate new $NH_3$ speed-emission curves for potential use in national emission inventories and transport models. Overall, this paper uses recent evidence to evaluate the complex mix of factors affecting $NH_3$ emissions from road vehicles. As the extent of fleet hybridisation, as well as the ageing and uptake of gasoline cars continues to evolve, the outcomes of this study improve the ability to assess the relative impacts of these changes on vehicle $NH_3$ emissions.

## 2. Materials and methods

### 2.1. Instrumentation

Vehicle emission remote sensing measurements were collected using two remote sensing devices: the Fuel Efficiency Automobile Test (FEAT) instrument developed by the University of Denver and the RSD5000 manufactured by Opus. The principle of operation is described extensively in the literature (Bishop and Stedman, 1996; Burgard et al., 2006a) and is only briefly considered here. The instrument setup consists of an UV/IR source, detector, optical speed bars and a vehicle registration plate camera. The UV/IR source and detector are aligned across a single lane road, at the level of the vehicle exhaust plume. As each vehicle intersects the UV/IR beam, the amount of light absorbed by each target pollutant at specific wavelengths of light is measured. Within the detector module there are four non-dispersive IR detectors to measure CO (4.6 μm), $CO_2$ (4.3 μm), hydrocarbons (HC, 3.4 μm) and a background reference (3.9 μm). Inside the FEAT detector the UV component is passed through a quartz fibre bundle to two separate spectrometers; one spectrometer measures $NH_3$ (209, 213 and 217 nm) and NO (227 nm) (Burgard et al., 2006b) and the other measures $NO_2$ (430–447 nm). The Opus spectrometer also measures $NH_3$ at 205 nm in addition to the wavelengths used by the FEAT. The Opus RSD5000 does not have a separate spectrometer for the detection of $NO_2$.

Each pollutant is measured as a ratio to $CO_2$, to account for the variation in the dilution and position of the exhaust plume. The molar volumes of each pollutant, e.g. $NH_3$ to $CO_2$, can be used to derive fuel-specific emission factors in grams of pollutant per kilograms of fuel. Calibrations are conducted every few hours using three calibration cylinders containing (1) propane, NO, CO and $CO_2$ in $N_2$, (2) $NH_3$ and propane in $N_2$, (3) $NO_2$ and $CO_2$ in synthetic air. This accounts for changes in instrument sensitivity and ambient $CO_2$ levels. Detailed cylinder specifications can be found in Table S1.

A photograph of each vehicle is taken to capture the registration plate. The vehicle registration numbers were cross-referenced with vehicle information databases by CDL Vehicle Information Services Limited to return data such as fuel type, Euro standard and vehicle manufacture and registration dates. CDL retrieve information from the Driver and Vehicle Licensing Agency as well as data queried from the Society of Motor Manufacturers and Traders Motor Vehicle Registration Information System. Information regarding the mileage of a vehicle at its last MOT (technical) inspection test was also made available by CDL.

### 2.2. Measurement locations

Vehicle emission remote sensing measurements were collected at 37 sites across 14 regions in the United Kingdom between 2017 and 2020. Detailed location information can be found in Table S2. Surveys were carried out during daylight hours (approximately 0800–1800 h), apart from during periods of rain as the instrumentation is not weatherproof. The ambient temperature ranged from −1 to 29 °C throughout the measurement campaigns, with a mean temperature of 14 °C, covering over 98% of air temperature conditions experienced (for example) in London. A total of 405,217 passenger car measurements were obtained. 49% of the measurements were gasoline vehicles and 3% were gasoline hybrids. A statistical summary of these records is provided in Table 1.

### 2.3. Cold start measurements

An important part of this study is a comparison between emissions from gasoline vehicles that are likely to have hot engines versus those with cold engines. For most remote sensing campaigns it is difficult to know the proportion of vehicles that may have undergone a cold start. However, with careful site selection, it is possible to set up a contrast between conditions where hot or cold engines are dominant. Vehicle emission measurements were made at the Harwell Science Campus, approximately 25 km south of the City of Oxford in south England, over 18 days between 20th March and 20$^{th}$ September 2017. The campus has over 5,000 employees and is isolated from any major towns and cities, therefore the vast majority of vehicles arriving in the morning would have hot engines given the distances they would have travelled. Conversely, most vehicles leaving the campus at the end of the day would have been parked for several hours and would be leaving the site with cold engines. The measurements were conducted at two exits of a roundabout on Fermi Avenue, allowing vehicles both entering and leaving campus to be measured. Both survey sites were on flat terrain with zero gradient and it is estimated that vehicles leaving the site would have typically travelled 300–500 m prior to their measurement. A total of 3,893 Euro 3–6 gasoline passenger cars were measured arriving at the site and 3,355 were measured leaving the site. A summary of the measurements is provided in Table 2 and shows that the distributions of

**Table 1**
Summary of gasoline and gasoline hybrid passenger car measurements. The number of manufacturers with ≥100 measurements is shown. [1]Mean (standard deviation).

| Characteristic | Gasoline | Gasoline hybrid |
|---|---|---|
| Number of measurements | 198,188 | 11,440 |
| Manufacturers | 42 | 8 |
| Mileage records | 98,023 (49%) | 5,803 (51%) |
| Euro 2 | 8,313 (4%) | 0 (0%) |
| Euro 3 | 37,917 (19%) | 162 (1%) |
| Euro 4 | 56,932 (29%) | 764 (7%) |
| Euro 5 | 50,954 (26%) | 6,157 (54%) |
| Euro 6 | 44,072 (22%) | 4,357 (38%) |
| Speed[1] (km $h^{-1}$) | 35.5 (10.9) | 33.7 (9.6) |
| VSP[1] (kW $t^{-1}$) | 5.1 (7.8) | 4.8 (7.2) |
| Ambient temperature[1] (°C) | 14.2 (4.9) | 12.5 (4.2) |

**Table 2**
Summary of Euro 3–6 gasoline passenger cars measured entering and leaving the Harwell Science Campus. [1]Mean (standard deviation).

| Characteristic | Arrive (hot) | Leave (cold) |
|---|---|---|
| Number of measurements | 3,893 | 3,355 |
| Euro 3 | 828 (21%) | 738 (22%) |
| Euro 4 | 1,373 (35%) | 1,116 (33%) |
| Euro 5 | 1,077 (28%) | 991 (30%) |
| Euro 6 | 615 (16%) | 510 (15%) |
| Speed[1] (km $h^{-1}$) | 35.1(4.5) | 31.9 (4.9) |
| Acceleration[1] (km $h^{-1}$ $s^{-1}$) | 1.9 (1.8) | 2.1 (2.8) |
| VSP[1] (kW $t^{-1}$) | 8.8 (5.9) | 8.8 (8.2) |
| Ambient temperature[1] (°C) | 13.0 (3.8) | 19.1 (2.7) |

vehicle speed and acceleration were similar for vehicles entering and leaving the site, yet ambient temperatures were different; vehicles leaving were measured later in the day and the average temperature was 19 °C, compared to around 13 °C in the morning.

### 2.4. Data analysis

Generalised Additive Models (GAMs) were used to derive relationships between emissions and variables such as vehicle mileage or vehicle specific power. GAMs are a highly flexible data-driven modelling approach that can be used to establish non-linear relationships between variables (Wood, 2004). The *gam* function in the mgcv R package was used in the current study (Wood, 2003). Quantile regression was also applied to determine how different percentiles of vehicle mileage vary with vehicle age. This was performed using the *qgam* function in the qgam R package (Fasiolo et al., 2017). An advantage of the GAM approach for these analyses is that prior data aggregation e.g. to the nearest 10,000 km for vehicle mileage, is not required, despite the individual vehicle measurements exhibiting considerable scatter.

### 2.5. Hybrid battery use

A measurement of emissions from a vehicle exhaust plume is attempted each time a vehicle passes the light beam of the remote sensing device. For conventional gasoline vehicles, a small fraction of measurements (1.7%) have an invalid $CO_2$ plume and are therefore discarded. This can occur for several reasons, such as only measuring a small part of the dispersing plume. However, the proportion of measurements with an invalid $CO_2$ plume is considerably greater for gasoline hybrid vehicles, because exhaust emissions are zero when the vehicle is using the battery. This means that the valid remote sensing measurements for hybrid vehicles represent emission behaviour when the vehicle is using the engine, but in reality overall emissions will be lower as the vehicles operate in battery mode for a proportion of each trip. In this study, we use the percentage of failed hybrid measurements, i.e. those with an invalid $CO_2$ plume, as a direct measure of the amount of time hybrids spend using batteries under real driving conditions. This information can be used to correct the measured $NH_3$ emission factors accordingly so that they represent trip-average emissions.

The percentage of time a vehicle spends using batteries can be influenced by driving conditions, therefore a GAM was used to predict the relationship between the percentage of failed measurements and vehicle specific power (VSP), for both conventional gasoline hybrids and PHEVs. VSP is an estimate of the power demand on the vehicle engine in kW $t^{-1}$ and was calculated using the method presented in Davison et al. (2020). Next, the GAM was used to predict the percentage of time a hybrid spends in battery mode at 2.9 kW $t^{-1}$. This is the average VSP under urban driving conditions, and is derived from over 1,394 km of 1 Hz real urban drive cycle data, obtained from measurements using portable emissions measurement systems (PEMS) performed by the UK Department for Transport (2016).

The average proportion of time spent using batteries under urban driving conditions was 29% for ordinary hybrid electric vehicles and 42% for PHEVs. Battery use under urban driving conditions was selected as the remote sensing surveys were conducted in urban areas. The average $NH_3$ emissions (g kg$^{-1}$ fuel) for hybrid electric vehicles and PHEVs were therefore reduced by 29% and 42% respectively, and as a result considered to more accurately represent trip-average $NH_3$ emission behaviour.

### *2.6. Distance-based emission factors*

Distance-based (g km$^{-1}$) emission factors for $NH_3$ were derived from the remote sensing measurements using the method presented in Davison et al. (2020) and GAMs were used to establish speed-emission factor curves. The g km$^{-1}$ emission factors were calculated over real-world drive cycles that encompass a wide range of driving conditions including urban, rural and motorway driving. The emission factors and speed-emission factor curves based on real world measurements can be compared with those in the COPERT emission factor model and the EMEP/EEA Emission Inventory Guidebook (EMISIA, 2018; Ntziachristos et al., 2019), which are typically based on a combination of laboratory and on-board measurements using PEMS.

In brief, the first step in the derivation of g km$^{-1}$ emission factors was the calculation of VSP, in kW t$^{-1}$. Road load values and aerodynamic drag coefficients provided in Davison et al. (2020) were used for this step. Next, fuel consumption was calculated from VSP using the linear relationship in the Passenger Car and Heavy Duty Emissions Model (Hausberger, 2003). Fuel consumption (kg s$^{-1}$) was then combined with the fuel-based (g kg$^{-1}$) emission factors from remote sensing to obtain time-specific emission factors in g s$^{-1}$.

GAMS were used to relate time-specific emission factors to VSP, categorised according to fuel type, Euro standard and engine size group. This enabled g s$^{-1}$ emissions to be mapped to 1 Hz drive cycles, obtained from PEMS measurements performed by the UK Department for Transport (2016). In total the PEMS data contains 4,243 km of real-world driving across 58 routes. The models were fit between 0 and 40 kW t$^{-1}$ and emissions from negative VSP conditions were assumed to be zero.

The g km$^{-1}$ emission factors can be calculated as the sum of all of the 1 Hz time-specific emissions divided by the total distance of all the drive cycles. For each Euro standard and engine size category, speed-emission factor curves were created for gasoline passenger cars using GAMs that relate g km$^{-1}$ emission factors to the range of vehicle speeds within the real-world drive cycles.

## 3. Results and discussion

### *3.1. Emissions from gasoline and gasoline hybrid cars*

Average fuel-specific (g kg$^{-1}$) $NH_3$ emissions by vehicle model year are shown for gasoline and gasoline hybrid passenger cars in Fig. 1. The size of the circles shows the number of measurements for each vehicle type and model year. Gasoline passenger cars make up a considerably larger share of the UK vehicle fleet compared to hybrids. Average $NH_3$ emissions from gasoline cars manufactured between 2000 and 2019 range from 0.42 to 1.11 g kg$^{-1}$. Overall a steady decrease in the amount of $NH_3$ emitted is observed with increasing model year, although this may be partly attributed to the age of the vehicle at the time of measurement, which is discussed later. A summary of the g kg$^{-1}$ $NH_3$ emissions, grouped by fuel type and Euro class, is provided in Table 3. The reported emission factors are considered highly robust, as they are based on around 210,000 gasoline and gasoline hybrid vehicles measured across a wide range of real driving conditions.

Two types of gasoline hybrid cars are shown in Fig. 1: conventional hybrid electric vehicles and plug-in hybrid electric vehicles (PHEVs). Overall hybrid vehicles make up a much smaller proportion of the fleet, but the amount of $NH_3$ emitted is non trivial and the fraction of hybrids in the vehicle fleet is anticipated to grow in the coming years. $NH_3$ is emitted from hybrid vehicles and detected by the remote sensing device when the vehicle is relying on the use of the internal combustion engine. $NH_3$ is not emitted when the vehicle is in battery mode. Therefore in reality, overall trip-average emissions of $NH_3$ are lower because a proportion of the vehicle km is driven in battery mode, and the reported emission factors need to be adjusted to account for this.

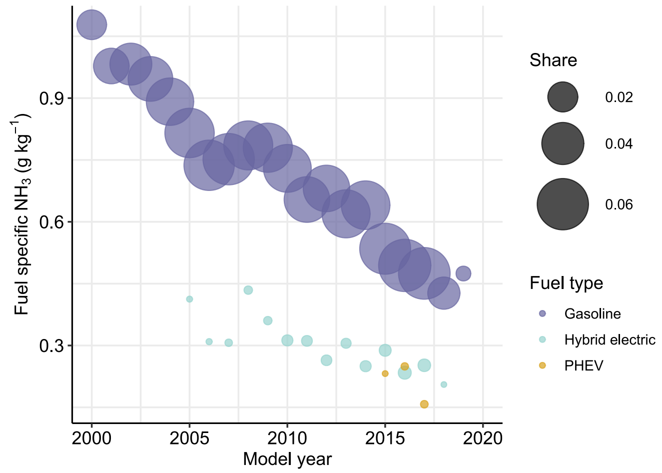


**Fig. 1.** Emissions of $NH_3$ (g kg$^{-1}$ fuel) for gasoline, hybrid electric and plug-in hybrid passenger cars by model year. The size of each point is proportional to the share of the vehicle type and model year in the total gasoline fleet. Emissions from hybrid electrics and plug-in hybrids are reduced by 29% and 42% respectively to account for the estimated percentage of time the vehicles are using batteries under urban driving conditions.

**Table 3**
Emissions of $NH_3$ (g kg$^{-1}$) from gasoline passenger cars, gasoline hybrid electrics and PHEVs, grouped by Euro standard. Measured emissions from hybrid electrics and PHEVs are reduced by 29% and 42% respectively to account for battery use in urban driving conditions. The associated uncertainties are based on the 95% confidence interval of the emission factors.

| Euro standard | Fuel specific $NH_3$ (g kg$^{-1}$) | | |
|---|---|---|---|
| | Gasoline | Hybrid electric | PHEV |
| 2 | 1.13 ± 0.04 | – | – |
| 3 | 0.93 ± 0.02 | – | – |
| 4 | 0.78 ± 0.01 | 0.13 ± 0.04 | – |
| 5 | 0.64 ± 0.03 | 0.32 ± 0.02 | 0.24 ± 0.13 |
| 6 | 0.49 ± 0.01 | 0.28 ± 0.04 | 0.20 ± 0.05 |

The $NH_3$ emissions for hybrid electrics and PHEVs shown in Fig. 1 have been reduced by 29% and 42% respectively, to account for the estimated amount of time the vehicles use batteries under typical urban driving conditions. This is estimated using the percentage of failed $CO_2$ remote sensing measurements for hybrids at VSP levels representative of urban driving. Overall, $NH_3$ emissions from hybrid cars are lower than gasoline cars. The average amount of $NH_3$ emitted from hybrid electric cars manufactured between 2005 and 2018 is 0.21–0.42 g kg$^{-1}$. Average $NH_3$ emissions from PHEVs manufactured between 2015 and 2017 range from 0.15 to 0.26 g kg$^{-1}$. $NH_3$ emissions by Euro class for hybrid vehicles are also included in Table 3. The measured emissions have been adjusted to account for battery use in urban driving conditions. The corresponding measured values (prior to adjustment) can be found in Table S3.

### *3.2. Hybrid battery use*

Fig. 2 shows the relationship between VSP and the estimated

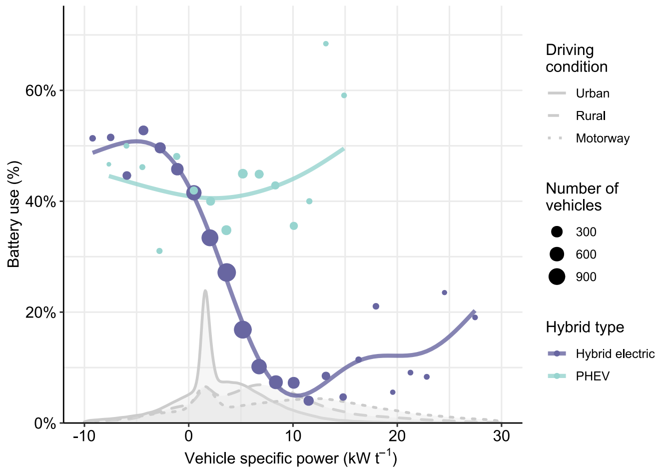


**Fig. 2.** Relationship between vehicle specific power and estimated percentage of time on batteries for gasoline hybrid electrics and PHEVs. The size of the circles shows the number of measurements. The density plots (grey) show the distribution of vehicle powers for urban, rural and motorway driving conditions observed in the Department for Transport PEMS tests.

percentage of time spent using batteries for hybrid electric vehicles and PHEVs. The size of the circles is proportional to the number of measurements. The density plots show the VSP distributions of the PEMS drive cycle measurements carried out by the Department of Transport and represent over 4,000 km of driving across 58 routes (Department for Transport, 2016). The distributions help visualise how expected battery use varies for different driving scenarios.

For hybrid electric vehicles, the proportion of time spent using batteries, also known as the utility factor, is high at low power demands. However a sharp decline is observed as the VSP increases. A different trend is observed for PHEVS, and the data suggests that these vehicles use their batteries across a wider range of driving conditions. This means that PHEVs extend their advantage over hybrid electrics in rural and motorway scenarios. For both vehicle types, an increase in utility factor occurs at the highest power demand; this may be a result of the increased need for battery use to compensate for the lower powered engines installed in hybrids.

Overall the predictions show that across all driving conditions, utility factors of 23% and 41% are estimated for conventional hybrid electrics and PHEVs respectively. The predicted battery use of 41% for PHEVs is similar to the value of 37% reported by the ICCT, obtained from their analysis of real-world $CO_2$ emissions performance of PHEVs (Plötz et al., 2020). Both the findings in this study and those presented by the ICCT show significantly lower battery use than results from NEDC type approval tests, which report a utility factor of 67% for PHEVs.

A key strength of this study is that the findings are based on direct observations from real driving measurements on UK roads. In the case of PHEVs, the results may indicate that people are not charging their vehicle often enough, or choosing a driver-selectable vehicle operating mode that blends battery/motor and engine use. The outcomes of this study have been used to correct the $NH_3$ emissions from hybrid vehicles to adjust the emissions measured by remote sensing when using an engine to account for zero exhaust emissions when using batteries. However, there are a number of applications for the failed $CO_2$ remote sensing measurements; for example this information may provide useful insight into the real world $CO_2$ emissions performance of hybrids. This information is useful for many countries, including the UK, who are committed to reaching net zero in terms of greenhouse gas emissions in the upcoming decades.

### 3.3. Emissions by vehicle mileage

Fig. 1 showed a decrease in $NH_3$ emissions from gasoline passenger cars with increasing model year. It is useful to consider if the observed decrease is because newer vehicles are inherently cleaner, or if it is due to the fact that earlier-model vehicles are older at the time of measurement, or some combination of both factors. The vehicle technical information allows the age of each vehicle at the time of measurement to be determined. Traditionally, this has been the best available proxy for studying the effect of vehicle deterioration on $NH_3$ emissions. More recently however, records of vehicle mileage at the vehicle's last MOT test have been made available. The MOT inspection is the UK's annual test of vehicle safety and roadworthiness. This is arguably a better measure of deterioration as it provides a direct measure of the distance a vehicle has driven and is therefore more representative of vehicle usage than vehicle age. This is because in reality, vehicles of a certain age will be associated with a wide range of mileages, depending on how far an individual vehicle is driven. The left panel of Fig. 3 shows the variation of vehicle mileage with vehicle age for UK gasoline passenger cars. The purple line shows the median value and the blue lines show the 5th and 95th percentile values determined by quantile regression. As an example, a 5-year old car has a median mileage of around 35,000 km, but the range from the 5th to 95th percentile is approximately 15,000 to 75,000 km. As vehicle age increases, the variation in the associated mileage becomes even greater.

The right panel of Fig. 3 shows emissions of $NH_3$ (g kg$^{-1}$ fuel) as a function of vehicle mileage for gasoline passenger cars, derived using a GAM. The relationship between emissions of $NH_3$ and mileage is based on over 73,000 gasoline passenger car measurements for which mileage information was available. Mileage information is only available for around half of the fleet because passenger cars in the UK are not required to undertake an annual MOT test until they are over 3 years old. Nevertheless, the large sample size and wide coverage of mileage range provide a valuable insight into the effect of vehicle deterioration on $NH_3$ emission behaviour. The GAM shows that as vehicle mileage increases, the amount of emitted $NH_3$ also increases, close to linearly. This is likely due to degradation of the air-fuel ratio control, causing fuel-rich conditions during which $NH_3$ is created in the catalyst. The GAM predicts an increase in the average amount of $NH_3$ emitted of around 0.3 g kg$^{-1}$ fuel over the first 100,000 km driven. The increase occurs at a linear rate of approximately 0.075 g kg$^{-1}$ per 25,000 km. The rate of increase in emitted $NH_3$ becomes more gradual at higher mileages (above around 120,000 km), although it is worth noting that there is more uncertainty in the GAM at very high mileages as there are fewer vehicle measurements available.

A unique strength of a database in which vehicle emission remote sensing data is matched with mileage information is that the sample size is large enough to compare average $NH_3$ emissions for different Euro class vehicles that have driven the same distance. For example, this study revealed that average $NH_3$ emissions associated with vehicles that have travelled between 40,000 and 50,000 km are 0.78 g kg$^{-1}$ fuel for Euro 3 and 4 gasoline passenger cars, and 0.68 g kg$^{-1}$ fuel for Euro 5 and 6 cars. This suggests that whilst vehicle deterioration leads to increasing $NH_3$ emissions over time, absolute emissions from newer Euro standards are also gradually decreasing.

Changes in $NH_3$ emission performance due to vehicle deterioration is a key consideration in the EMEP/EEA emission inventory guidebook (Ntziachristos et al., 2019), which is used to inform the COPERT emission factor model (EMISIA, 2018) as well as national inventories in many European countries. COPERT emission factors for $NH_3$ are a function of cumulative mileage and are based on mean odometer readings for vehicles of a particular type. Between 0 and 100,000 km, the COPERT $NH_3$ emission factors for gasoline cars increase by 15% for Euro 3 and 4 and by 18% for Euro 5 and 6 under hot urban driving conditions. In this study, a direct measure of the rate of increase in $NH_3$ emissions with vehicle mileage under real driving conditions is available for

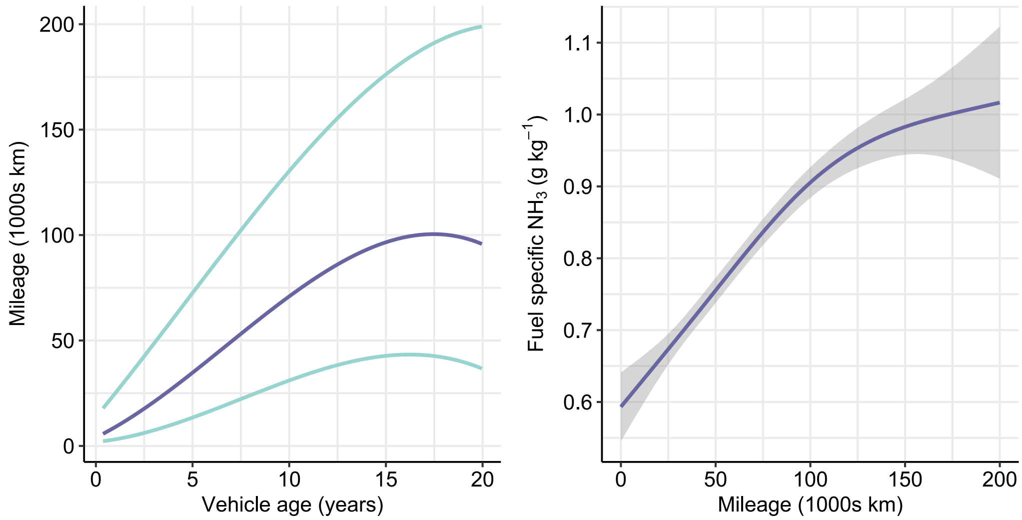


**Fig. 3.** Variation of vehicle mileage with vehicle age for gasoline passenger cars in the UK (left). The purple line shows the median value and the blue lines show the 5th and 95th percentile values as determined by quantile regression. Emissions of $NH_3$ (g $kg^{-1}$ fuel) as a function of vehicle mileage for gasoline passenger cars, derived using a GAM (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

comparison. For Euro 3 and 4 gasoline passenger cars, we observe that $NH_3$ emissions increase by around 35% between 0 and 100,000 km. This is a higher rate of increase than assumed in the EMEP/EEA emission inventory guidebook. For Euro 5 cars, $NH_3$ increases by approximately 17% over the first 100,000 km, which agrees well with the COPERT assumptions. There is insufficient mileage data for Euro 6 cars at this stage. Overall, this study uses a large number of measurements conducted under real driving conditions to strengthen the understanding of $NH_3$ emission behaviour in relation to vehicle deterioration.

### 3.4. Cold start effects

Exhaust emissions that occur before a vehicle's engine and after-treatment system have reached the normal operating temperatures are referred to as cold start emissions. Fig. 4 shows emissions of $NO_x$ and $NH_3$ from gasoline passenger cars, grouped according to Euro class and categorised by whether vehicles are likely to have hot or cold engines at the time of measurement. The $NO_x$ and $NH_3$ emission values are also provided in Tables S4 and S5. In line with expectations, $NO_x$ emissions decrease significantly with increasing Euro class. This is a result of the requirement for vehicle manufacturers to meet increasingly stringent $NO_x$ emission limits. Nevertheless, for Euro 3–5 gasoline cars, the amount of $NO_x$ emitted when the engine is cold remains higher than hot engine emissions. There is a clear reduction in the magnitude of the difference between cold start and hot exhaust $NO_x$ emissions with increasing Euro class. The cold start $NO_x$ is approximately a factor of 1.7 times higher for Euro 3 gasoline cars, whereas $NO_x$ emissions from Euro 6 cars are roughly similar for cold start and hot exhaust vehicles; the improved cold-start performance is likely a result of continuous improvements in catalyst light-off approaches.

$NH_3$ emissions from gasoline cars with hot engines are just below 0.6 g $kg^{-1}$ for Euro 3 and 4 vehicles, and approximately 0.3 g $kg^{-1}$ for Euro 5 and 6. With the exception of Euro 3 vehicles, cold start $NH_3$ emissions are higher than the warm engine emissions for each Euro class. However, unlike $NO_x$ emissions, the magnitude of the difference between emissions from cold and hot engines does not improve for the more recent Euro classes. The ratio of $NH_3$ emitted from cold versus hot engines is approximately 2.8 for Euro 5 vehicles and around 2.3 for Euro 6. During the engine warm-up phase, excess fuel is delivered to the engine to compensate for the loss of fuel as a result of condensation on cold

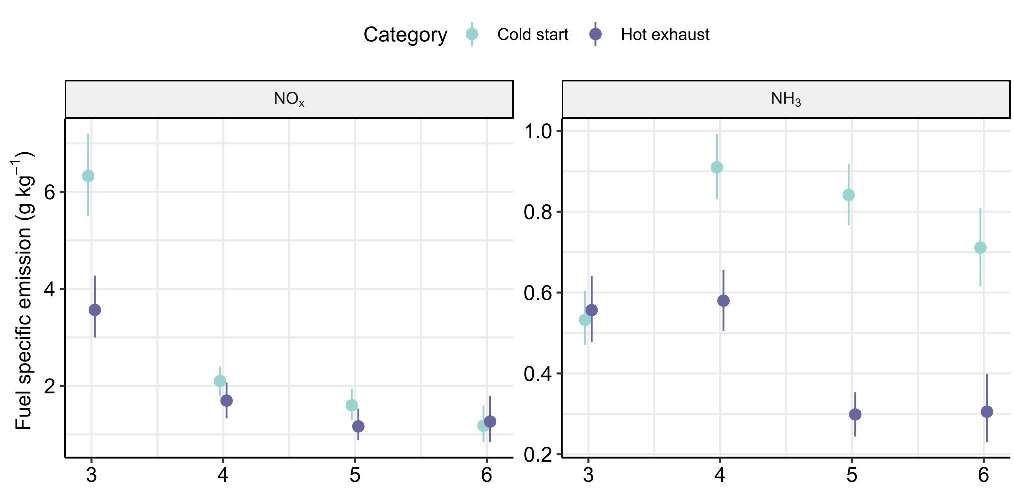


**Fig. 4.** Emissions of $NO_x$ and $NH_3$ (g $kg^{-1}$ fuel) from Euro 3–6 gasoline passenger cars, split by whether vehicles are likely to have hot engines or cold starts.

surfaces within the engine. This avoids engine misfire and maintains vehicle driveability (Boulter and Latham, 2009). Excess fuel equates to a decreased air-fuel ratio, which can lead to increased emissions of CO and hydrocarbons as a result of incomplete fuel combustion. Whilst the fuel rich conditions are beneficial for minimising cold start $NO_x$ emissions, $H_2$ formation can occur from CO and $H_2O$ via the water gas shift reaction of from hydrocarbons via steam reforming (Whittington et al., 1995; Barbier and Duprez, 1994). This has the unintended negative consequence of promoting the formation of excess $NH_3$ on vehicle start-up.

The amount of time a vehicle takes to reach its normal operating temperature depends on several factors, including ambient temperature, the length of time a vehicle has been parked for, and the extent to which a vehicle has been fully warmed up during its previous journey (Boulter and Latham, 2009). In this study, the average ambient temperature was 14 °C when vehicles with hot engines were measured, and 20 °C when the cold engines were measured. The measurements provide useful insight into cold start $NH_3$ emissions under real driving conditions, but in reality the amount of $NH_3$ emitted from cold starts is likely greater in certain situations, such as during the winter when ambient temperatures are lower. Furthermore, the meteorological conditions associated with low ambient temperatures are generally less favourable for pollutant dispersion. This is particularly important in urban areas, where the majority of car journeys begin. In towns and cities, $NH_3$ emissions potentially have a more effective pathway to particle formation; a key consideration from a human exposure perspective as the population density is greater in towns and cities.

### 3.5. Emissions by vehicle manufacturer

Emissions of $NH_3$ (g kg$^{-1}$ fuel) for Euro 5 gasoline and gasoline hybrid passenger cars, categorised by the main vehicle manufacturer groups, are shown in Fig. 5. The width of each rectangle represents the share of the manufacturer group in each fleet. Note that the $NH_3$ emissions shown for hybrids are representative of when the vehicle is using the engine, and for this example $NH_3$ emissions have not been reduced to account for when the hybrid is using batteries. To assess the influence of manufacturer group composition on $NH_3$ emissions from gasoline and hybrid cars, Euro 5 vehicles have been selected, so that the average age of vehicles at the time of measurement is similar for both fleets. A comparison of the entire gasoline versus hybrid fleet would not be suitable as overall the hybrid fleet is newer.

The manufacturer grouping is based on the approach used by the International Council on Clean Transportation in their analysis of vehicle emission remote sensing data (Bernard et al., 2018). The grouping relies on the tendency for manufacturers to use similar aftertreatment technologies and emission control strategies in a range of vehicle models and across brands of the same vehicle 'family'. For example, the Toyota group includes Toyota, Lexus and Daihatsu vehicles. The manufacturer grouping for the main gasoline and gasoline hybrid passenger car manufacturers is provided in Table S6. For Euro 5 gasoline hybrid passenger cars, there are 2 main manufacturer groups as shown in Fig. 5, and the fleet is dominated by vehicles from the Toyota Group (TOY), which make up 90% of all measured Euro 5 gasoline hybrids. In contrast, there are 11 main manufacturer groups for Euro 5 gasoline cars and the proportions of the different groups are more evenly distributed; vehicles from the RNA, FRD, GEM and VWG groups each comprise between 12% and 19% of the sampled Euro 5 gasoline car fleet for example.

Before adjustments are made to account for the fact that hybrid vehicles spend a proportion of their time using batteries, average $NH_3$ emissions from hybrid electric cars are already lower than those of gasoline cars; average emissions for Euro 5 vehicles are 0.45 g kg$^{-1}$ for hybrids and 0.65 g kg$^{-1}$ for gasoline cars. Fig. 5 indicates that this is likely due to the manufacturers involved, rather than an intrinsic characteristic of hybrids when their engine is in use. The bulk of Euro 5 hybrid vehicles are manufactured by the Toyota Group (90%) and the Honda Group (9%), with average $NH_3$ emissions of 0.47 and 0.21 g kg$^{-1}$ respectively. Interestingly, $NH_3$ emissions from gasoline cars produced by these two manufacturer groups are on the lower end of the scale (0.39 g kg$^{-1}$ for both Toyota and Honda), along with other groups such as FCA and GEM. Overall however, these lower-emitting manufacturer groups make up a smaller proportion of the total Euro 5 gasoline car fleet compared to the hybrid fleet. The higher overall $NH_3$ emissions associated with Euro 5 gasoline cars is driven by other higher emitting manufacturer groups such as RNA and BMW. These manufacturer groups do not produce a significant quantity of hybrid vehicles. Vehicle emission remote sensing provides a unique insight into manufacturer fleet mixes and suggests that the manufacturer composition of the fleet plays an important role in the quantity of $NH_3$ emissions from road vehicles.

### 3.6. Distance-specific emission factors

In the EMEP/EEA approach for preparing national emission inventories, emissions are scaled to either single average speeds representative of urban, rural and highway roads, or to mean speed distribution curves (Ntziachristos et al., 2019). Vehicle speed is selected as an appropriate metric because the data is readily available. The speed-emission equations are usually generated by deriving average emissions from several drive cycles performed at different speeds and

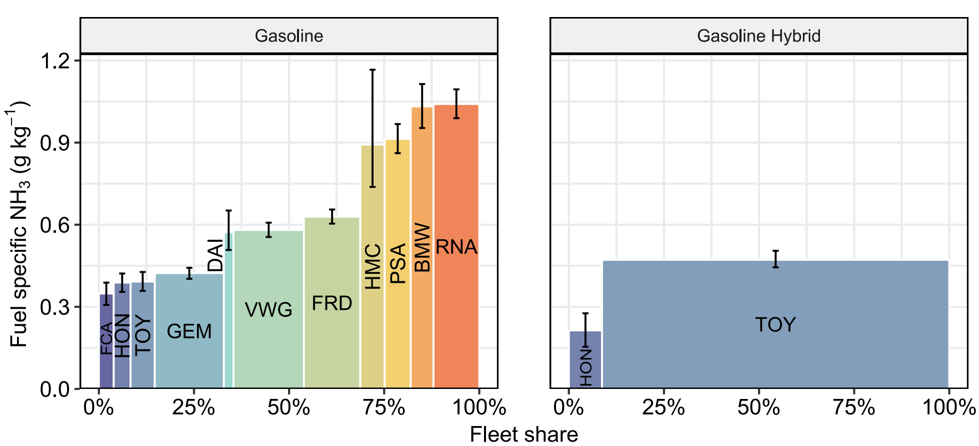


**Fig. 5.** Emissions of $NH_3$ (g kg$^{-1}$ fuel) for Euro 5 gasoline and gasoline hybrid passenger cars by manufacturer group. The rectangle width represents the share of the manufacturer group in each fleet. $NH_3$ emissions from gasoline hybrid cars have not been adjusted to account for estimated time spent using batteries. The error bars show the 95% confidence interval in the mean.

fitting a curve to the data.

In this study, we use remote sensing measurements and apply the method developed by Davison et al. (2020) to generate speed-emission curves based on real driving data. The advantage of this approach is that the speed-emission curves are based on a large number (> 200,000) of on-road $NH_3$ emission measurements across a wide range of vehicle speeds, representative of vehicles in the existing UK fleet. The speed-emission relationships also account for the amount of vehicle km driven and reflect the condition, or state of repair, of the vehicles on UK roads between 2017 and 2020.

Fig. 6 shows the calculated speed-emission curves for $NH_3$ and $NO_x$ emissions from Euro 2–6 gasoline cars, separated into three vehicle engine size groups. A summary of the average distance specific emissions of $NH_3$ and $NO_x$ for a range of vehicle speeds can be found in Tables S7 and S8. Unlike $NO_x$ emissions, which show a clear decrease with increasing Euro class, $NH_3$ emissions are more persistent although small reductions are observed for newer vehicles. Furthermore, $NH_3$ emitted from gasoline cars with engine sizes greater than 1.4 L are generally slightly higher than from vehicles with engines less than 1.4 L. Importantly it is found that the greatest $NH_3$ emissions are associated with speeds less than around 35 km $h^{-1}$; this is likely a result of fuel enrichment during transients that typically occur at lower speeds. This is a key consideration for urban areas.

Speed-emission curves are a useful way to consider how emissions vary with traffic conditions in national inventories and this study provides a key contribution, particularly for $NH_3$ as existing data is limited. However, in reality the variability in emissions at any given speed is high. This means that the speed-emission curves are less useful on local scales or for specific points on a road as there are many other factors that influence a vehicle's emission, such as vehicle specific power, the level of congestion and the number of stop-starts.

## 4. Conclusions

This study provides new insight into $NH_3$ emissions from gasoline and gasoline hybrid cars under real driving conditions. The comprehensive nature of the vehicle emission remote sensing measurements allows many factors affecting $NH_3$ emissions to be evaluated. Using vehicle mileage data, we are able to investigate the effect of vehicle deterioration on $NH_3$ emissions behaviour. A key finding is that $NH_3$ emissions from gasoline passenger cars increase with increasing mileage. Furthermore, taking account of vehicle mileage, it is found that absolute $NH_3$ emissions are gradually decreasing with increasing Euro class. Since the 2015 dieselgate scandal, there has been a considerable increase in the sale of gasoline vehicles at the expense of diesel. In a previous study, g km$^{-1}$ $NH_3$ emissions from Euro 6 diesel cars were found to be approximately 30 times lower than the equivalent Euro 6 gasoline cars (Farren et al., 2020). This could have a significant influence on $NH_3$ emissions from road transport, given the dominance of emissions from gasoline vehicles, and the fact that emissions will increase as the vehicles age.

In this study we are also able to quantify the $NH_3$ cold start penalty for gasoline passenger cars. It is found that for Euro 5 and 6 vehicles, cold start $NH_3$ emissions are a factor of approximately 2.5 times higher than hot exhaust emissions. This is a key consideration in urban areas, where most cold starts occur and the pathway to $PM_{2.5}$ formation is potentially more efficient. Detailed air quality modelling would be useful in the future to quantify the effect of $NH_3$ emissions from road vehicles in urban areas on $PM_{2.5}$ formation.

New insight into hybrid vehicle behaviour is also presented. We demonstrate a new method, which relies on the percentage of failed $CO_2$ remote sensing measurements as a direct measure of the proportion of time hybrid vehicles use batteries across a range of driving conditions. In this study, the method is used to adjust the measured $NH_3$ emissions when the engine is in use, to obtain trip-average emission factors. A possible risk associated with some hybrid vehicles is excess exhaust emissions as a result of aftertreatment cooling when the vehicle is using its battery, which may occur more rapidly than when the vehicle is stationary due to exhaust flow through the catalyst; the data presented here however does not show a penalty in terms of $NH_3$ emissions for

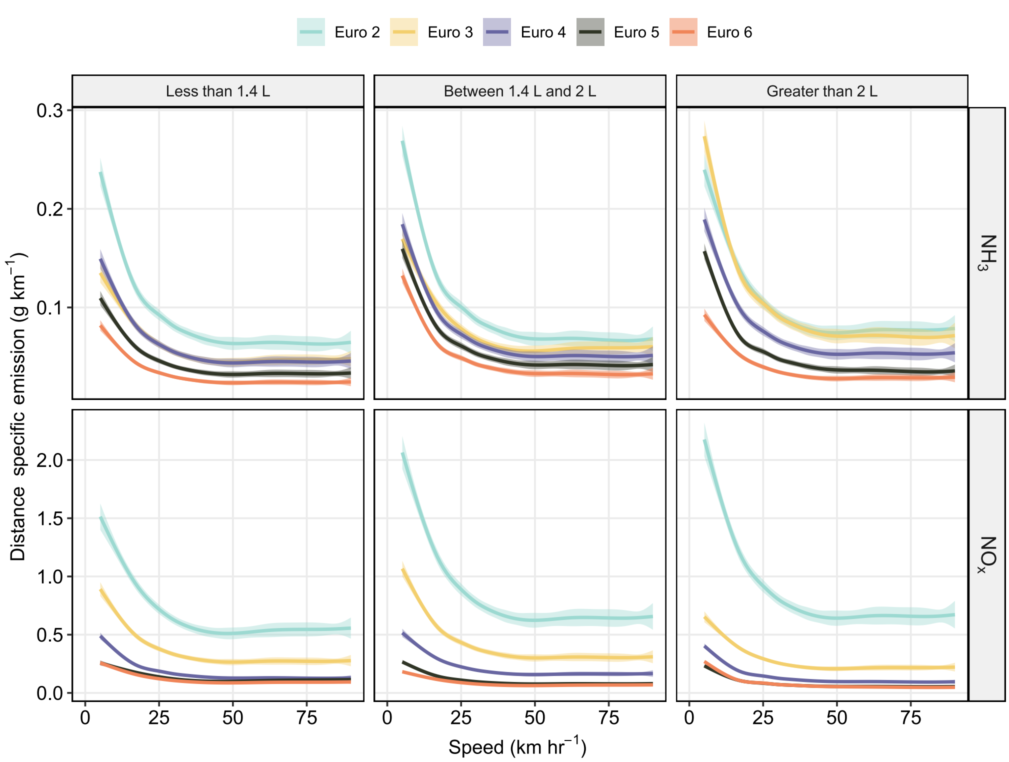


**Fig. 6.** $NH_3$ and $NO_x$ speed-emission curves, for Euro 2–6 gasoline passenger cars, categorised according to vehicle engine size. The curves are derived using GAMS.

hybrid vehicles. The method can potentially be used for a wider range of applications, such as to assess the real world $CO_2$ emissions performance of hybrids. This is timely and valuable as increased hybridization of the vehicle fleet is anticipated in upcoming years as countries work to reduce greenhouse gas emissions and meet their net zero targets.

Finally, the $NH_3$ emission factors for gasoline cars obtained from the remote sensing data are used to establish new speed-emission curves based on real driving data. These relationships are valuable as speed-emission curves are used widely in national inventories to assess the influence of traffic conditions on emissions, yet the data currently available for $NH_3$ is limited. Furthermore, work is being carried out in Europe to develop Euro 7/VII emission standards (AGVES, 2019) and a number of currently unregulated emissions, such as $NH_3$, nitrous oxide and methane, will be considered. The existing Real Driving Emissions legislation, which involves on-road PEMS testing in addition to laboratory measurements, should minimize discrepancies between the laboratory and on-road performance. Nevertheless, this study is timely as it provides $NH_3$ emission factors based on real driving data, in addition to new information on the factors affecting $NH_3$ emissions from gasoline and gasoline hybrid cars.

## CRediT authorship contribution statement

**Naomi J. Farren:** Conceptualization, Investigation, Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **Jack Davison:** Investigation, Visualization, Methodology, Formal analysis, Writing – review & editing. **Rebecca A. Rose:** Conceptualization, Investigation, Methodology, Formal analysis, Writing – review & editing. **Rebecca L. Wagner:** Investigation, Writing – review & editing. **David C. Carslaw:** Conceptualization, Investigation, Methodology, Formal analysis, Writing – review & editing, Funding acquisition, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aeaoa.2021.100117.

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