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Farren, Naomi J. orcid.org/0000-0002-5668-1648, Davison, Jack, Rose, Rebecca A. et al. (2 more authors) (2020) Underestimated Ammonia Emissions from Road Vehicles. Environmental Science and Technology. 15689–15697. ISSN: 1520-5851

https://doi.org/10.1021/acs.est.0c05839

Underestimated ammonia emissions from road vehicles

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The published version of this article is available here.

To cite please use: Farren, N.J., Davison, J., Rose, R.A., Wagner, R.L. and D. C. Carslaw (2020). Underestimated ammonia emissions from road vehicles. *Environmental Science & Technology*, 54, 15689–15697, https://dx.doi.org/10.1021/acs.est.0c05839.

Abstract

In this study we use comprehensive vehicle emission remote sensing measurements of over 230,000 passenger cars to estimate total UK ammonia (NH_3) emissions. Estimates are made using 'top-down' and 'bottom-up' methods that demonstrates good agreement to within 1.1% for total fuel consumed or CO_2 emitted. A central component of this study is the comprehensive nature of the bottom-up emission estimates that combines highly detailed remote sensing emission data with over 4,000 km of 1-Hz real driving data. Total annual UK NH_3 emissions from gasoline passenger cars is estimated to be 7.8 ± 0.3 kt from the 'bottom-up' estimate compared with 3.0 ± 1.7 kt reported by the UK national inventory. An important conclusion from the analysis is that both methodologies confirm that gasoline passenger car NH_3 emissions are underestimated by a factor of about 2.6 compared with the 2018 UK National Atmospheric Emissions Inventory. Furthermore, we find that inventory estimates of urban emissions of NH_3 for passenger cars are underestimated by a factor of 17.

Introduction

Ammonia (NH_3) emissions contribute significantly to the formation of fine particulate matter ($PM_{2.5}$) in the atmosphere and nitrogen deposition in ecosystems. This means that NH_3 plays a central role in the impact of air pollution on human health and the environment, and efforts to better understand and control NH_3 emissions are essential. Gaseous NH_3 is relatively short-lived in the atmosphere; it is either deposited back to terrestrial surfaces by dry deposition or it reacts rapidly with acidic pollutants (e.g. nitric and sulphuric acid) to form compounds such as ammonium nitrate and ammonium sulphate.[1] Particulate ammonium (NH_4^+) persists for longer in the atmosphere and can be transported long distances (several hundred km) before being deposited, primarily by rain or snow as wet deposition.[2] Therefore the deposition of NH_3 and NH_4^+ has impacts on both local and international (transboundary) scales and is considered a main contributor to the widespread exceedance of critical loads for eutrophication and reduction of plant biodiversity.

In 2019, the UK government released its Clean Air Strategy, which sets out the actions needed to tackle air pollution and reduce the impact on human health and the environment.[3] This strategy recognises the important role emissions of NH_3 play and the actions needed to reduce agricultural NH_3 emissions are covered extensively. In 2018, agricultural activities were estimated to contribute to 84% of total UK NH_3 emissions.[4] However, there are additional sources of NH_3 aside from agriculture, including emissions from road vehicles. Vehicular NH_3 emissions are co-emitted with nitrogen oxides (NO_x) and may have a more effective pathway to particle formation in urban environments, compared to NH_3 from agricultural activities which tends to be emitted in rural, low-NO_x regions. Recent research suggests that emissions of vehicular NH_3 and NO_x can lead to transient, inhomogeneous conditions in urban environments, whereby the gas-to-particle ammonium nitrate system is out of equilibrium and gas-phase supersaturations are sustained. This process can drive the rapid growth of new particles, enabling newly formed particles to survive scavenging losses in highly polluted environments.[5] The enhanced pathway to particle formation is also supported by 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.[6]

There are two main sources of NH_3 emissions from road vehicles — catalyst-equipped gasoline vehicles, and light and heavy-duty diesel vehicles that rely on selective catalytic reduction (SCR). In both cases, NH_3 is not released directly from the internal combustion engine, instead it is formed as an unintended consequence of the technologies introduced to reduce NO_x emissions. In Europe, three-way catalysts (TWCs) first came into force for gasoline vehicles in 1993 with the introduction of the Euro 1 emissions standard[7] and operate by simultaneously oxidising carbon monoxide (CO) and unburnt hydrocarbons (HCs) to CO_2 and water while reducing NO_x to nitrogen gas. Ammonia formation can occur in the TWC as a result of the reduction of nitric oxide (NO) by hydrogen (H_2),[8] which is generated from CO and H_2O via the water-gas-shift reaction or from hydrocarbons via steam reforming.[9,10] The generation of H_2 is favoured under fuel-rich conditions, and may remain stored on the catalyst, available for the reduction of subsequent NO emissions. SCR is a diesel vehicle after-treatment system aimed at reducing NO_x emissions by reacting NO and NO_2 with NH_3 on a catalyst surface. The NH_3 comes from the injection of urea, which must be carefully managed; injection of excessive quantities of NH_3, low temperatures in the system, and catalyst degradation are contributing factors that may lead to excess NH_3 emissions, commonly termed 'ammonia slip'.[8]

Whilst emissions of NO_x have been regulated effectively in many countries, less attention has been paid to NH_3 and the reduction in emissions has been slow or insignificant. This is in part due to lack of regulation; with the exception of the Euro VI standard on heavy duty diesel vehicles, there are no vehicle emission standards to regulate NH_3 worldwide.[11] In the US, NH_3 is rapidly becoming the most dominant reactive nitrogen compound emitted from many newer vehicles, due to the growing efficiency of TWCs to reduce NO_x emissions and the introduction of SCR.[12]

Global NH_3 emissions from the transportation sector are thought to be highly underestimated.[13] Sun et al. (2017) used mobile laboratory observations to derive NH_3 emissions from US vehicles and found that emissions were more than twice those of the National Emission Inventory.[14] The proportion of gasoline vehicles in the fleet is lower in the UK and across Continental Europe compared to the US, therefore the vehicular contribution to total NH_3 is expected to be lower. However, in Europe, the higher proportion of light duty diesel vehicles and the associated NO_x emissions means that there are potentially highly effective pathways to ammonium nitrate and $PM_{2.5}$ formation. In other words, the sensitivity of particle formation and nitrogen deposition to vehicle NH_3 emissions in Europe is theoretically very significant. According to the UK National Atmospheric Emissions Inventory (NAEI), total NH_3 emissions from road transport were estimated to be 4.4 kt in 2018, accounting for 1.6% of total UK NH_3 emissions.[15] However, this estimate is based on emission factors derived from a limited number of vehicles tested in the laboratory and until recently there has been very few measurements available for vehicular NH_3 emissions under real-world driving conditions.

To address the considerable lack of real-world emissions data on NH_3 from road vehicles, the current work uses highly detailed and comprehensive vehicle emission remote sensing measurements to derive new emission factors for the passenger car fleet. An important aim of the work is to develop both a 'top-down' and 'bottom-up' method to calculate UK total emissions of CO_2 and NH_3 that can be compared with the UK NAEI and fuel sales statistics. Of most significance is the comprehensive approach adopted to calculate bottom-up emission estimates that combines both real driving emission measurements and driving activity patterns to address some of the common limitations of emissions inventory development. The robustness of the approaches developed are assessed by considering the total carbon / energy balance. Finally, we provide new UK total NH_3 estimates and consider the wider atmospheric impacts of these estimates.

Materials and methods

Instrumentation

Two spectroscopic remote sensing (RS) instruments were used to measure vehicle emissions: the Fuel Efficiency Automobile Test (FEAT) instrument developed by the University of Denver and the Opus AccuScan RSD 5000. The development and operation of the FEAT instrument has been described extensively in the literature.[16] The instrument consists of a source and detector aligned across a single lane road. The source is a collinear beam of infrared (IR) and ultraviolet (UV) light, which is separated into the IR and UV components by a dichroic beam splitter when it enters the detector. There are four non-dispersive IR detectors to measure CO (3.6 µm), CO_2 (4.3 µm), hydrocarbons (HC, 3.4 µm) and a background reference (3.9 µm). The UV component passes through a quartz fibre bundle to two separate UV spectrometers; one spectrometer measures SO_2, NH_3 and NO (200-226 nm) and the other measures NO_2 (430–447 nm). Unlike the FEAT instrument, the Opus RSD 5000 does not have a separate spectrometer for the detection of NO_2.

A measurement of the exhaust plume is triggered each time a vehicle passes the instrument setup. All species are quantified as a ratio to CO_2, to account for the large variation associated with the dilution and position of the vehicle exhaust plume. The ratio of each species is scaled according to certified gas cylinder ratios, which are measured every few hours. This accounts for variations in instrument sensitivity and ambient CO_2 levels, which are influenced by local CO_2 sources and atmospheric pressure. Three calibration cylinders are used at each measurement site 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. Full details of the cylinder specifications for the FEAT and Opus RSD 5000 can be found in Table S1. A measurement of the vehicle speed and acceleration is provided by speed bar lasers and a video camera is used to photograph each vehicle registration plate.

Vehicle emission remote sensing measurements provide a direct measure of the molar volume of a pollutant e.g. NH_3 to CO_2, from which fuel-based emission factors in $\mathrm{g\,kg^{-1}}$ can readily be derived. However, of more interest in the current work are distance-based emission factors in $\mathrm{g\,km^{-1}}$ that can be used to estimate total UK emissions of NH_3. The calculation of $\mathrm{g\,km^{-1}}$ emissions from $\mathrm{g\,kg^{-1}}$ requires an estimate of the fuel consumption of a vehicle at the time it was measured, which is an issue that is considered in more detail later.

Vehicle technical information

The vehicle registration plate images were digitised and sent to a commercial supplier (CDL Vehicle Information Services Limited) to obtain technical information for each individual vehicle. The information details physical characteristics of the vehicle itself (e.g. engine size, fuel type) as well as the Euro Standard and vehicle manufacture and registration dates. The information provided by CDL is retrieved from both data collected by the Driver and Vehicle Licensing Agency as well as data queried from the Society of Motor Manufacturers and Traders Motor Vehicle Registration Information System. Data were also obtained from CDL relating to the mileage of a vehicle at its last annual MOT (technical) inspection test. The mileage and the date of inspection for passenger cars and Light Commercial Vehicles (LCV, N1 Type Approval category) greater than three years old was available (vehicles less than three years old are not required to undertake an annual MOT inspection). Although the recorded mileage is that at the time of the MOT inspection, rather than the actual time of measurement, the mismatch in MOT date and measurement date is small ($<$ 12 months in all cases).

Measurement locations and vehicles

Vehicle emission RS surveys were conducted at 37 sites across 14 regions in the United Kingdom between 2017 and 2020. Further details of the measurements locations can be found in Table S2. A total of 318,248 valid NH_3 measurements were collected, of which 124,668 and 110,109 were gasoline and diesel passenger cars, respectively. Data from approximately 200 vehicle manufacturers were recorded. For safety reasons, and to ensure the spectroscopic measurements were valid, surveys were carried out on weekdays during daylight hours (0800 – 1800 h) apart from during periods of rain. Ambient temperature during the surveys ranged from -1 to $29\,^{\circ}$C, with a mean temperature of $14\,^{\circ}$C and covering over 98% of air temperature conditions experienced (for example) in London. The mean vehicle speed for valid passenger car measurements was 35.3 $\mathrm{km\,h^{-1}}$ with a standard deviation of 9.7 $\mathrm{km\,h^{-1}}$.

While the vehicle emission remote sensing measurements contain valuable information on the emissions of different types of vehicle, the data also provides important information that can be used as the basis to calculate total UK emissions. For example, the recorded mileage (from the annual technical inspection) of over 200,000 vehicles provides a robust way in which to quantify total annual mileage by fuel type, Euro standard and so on. The counts of vehicles from the measurement surveys, which are conducted over a wide range of urban areas in the UK (Table S2), provide a direct measurement of the relative share of distance vehicles drive under urban driving conditions. The latter measurement is of direct relevance for estimating the share of vehicle km driven by fuel type and also accounts for the lower annual mileages of older vehicles.

Methods to estimate total vehicular NH_3 emissions

There are two main approaches used in the compilation of emission inventories, referred to as 'top-down' and 'bottom-up'. The top-down approach typically starts with quantities such as total fuel use at a national level, which is then apportioned to smaller geographic scales. In the bottom-up approach, data are generally used at a local scale and then aggregated to a national scale. For example, emission factors for individual vehicle types can be combined with activity data such as annual vehicle km, together with some account of driving conditions, to derive a total annual emission. Both approaches have merit and often the approach used is determined by the availability of data. In inventories such as the UK NAEI, the top-down approach is used to estimate emissions at finer spatial scales down to 1 $\mathrm{km^2}$. However, a bottom-up approach has the advantage of providing a way in which to calculate emissions at sub-national scales e.g. urban areas, which is a characteristic exploited in this work.

The combined use of top-down and bottom-up approaches can provide an effective means of inventory verification and a check on whether there is consistency between two different methods to estimate the same quantity. The effectiveness of using the two approaches in quantifying emissions totals depends on the pollutant and emission sector in question. In the current context, the focus is on gasoline emissions of NH_3. The top-down approach starts with an estimate of total UK gasoline fuel sales, which is a quantity known to high accuracy. The advantage of considering vehicular gasoline is that its use is strongly dominated by a single sector of passenger cars, accounting for 97% of UK vehicular fuel consumption, with minor contributions from gasoline use in motorcycles and LCVs.[17] Conversely, diesel fuel is used in a wide range of vehicle types (e.g. passenger cars, LCVs and heavy duty vehicles). Considering emissions from diesel vehicles therefore includes an extra step of allocating total fuel sales between types of vehicle, which introduces additional uncertainty.

In reality, there can be considerable differences between top-down and bottom-up estimates. Trombetti et al.[18] for example, showed that substantial differences in terms of total emissions, sectorial emission shares and spatial distribution exist between the top-down and bottom-up datasets. Similarly, Pallavidino et al.[19] observed large differences between the two methods for a region in Italy, finding that differences in the vehicle fleet and vehicle mileages had an important impact on the outcome of emission estimates. Ideally, the comparison between the top-down and bottom-up approaches would result in the same estimate of total emissions of NH_3 at a UK national scale. Importantly, it would be hoped that the two methods would also yield similar estimates of total fuel consumed and CO_2 emissions. The latter point is important in terms of energy and carbon balance. Given the number of steps and data sources used in these calculations (particularly the bottom-up approach), there are numerous potential sources of discrepancies that can affect the similarity of emission estimates between the two methods.

Top-down estimate

An overview of the top-down calculation is shown by the series of purple shaded boxes in Figure 1. The top-down estimate of NH_3 emissions from gasoline passenger cars begins with a calculation of annual fuel consumption, which is based on total annual fuel sales data provided in the Digest of UK Energy Statistics.[20] This data set is published on an annual basis by the Department for Business, Energy and Industrial Strategy. A small correction is made for consumption by off-road vehicles and fuel consumed by the Crown Dependencies. In 2018, it was estimated that 3.8% of gasoline was consumed by inland waterways and off-road vehicles and machinery, and 0.5% was used in the Crown Dependencies.[21] A further adjustment is made to account for the fact that a minor fraction (approximately 3%) of the gasoline sold is used by motorcycles and gasoline LCVs, rather than passenger cars.[17]

The estimate of the annual mass of gasoline used by passenger cars can be combined with NH_3 remote sensing measurements to generate a top-down estimate of total annual UK NH_3 emissions from gasoline passenger cars (E_{NH_3}), as shown in Equation 1. The annual mass of gasoline used by passenger cars is represented by m (kg) and is multiplied by 3.135 to convert to the kg of CO_2 produced per kg of gasoline. This value is based on a review of the value for the carbon content of petrol used in the UK, provided by the UK Petroleum Industry Association, which states that the carbon content of gasoline is 855 gC/kg fuel.[21,22] To account for additional CO_2 produced from bioethanol blended with gasoline, the mass of CO_2 is multiplied by 1.032. This is necessary because the fuel sales figures represent the fossil fuel component only and do not account for the fact that gasoline in the UK contains up to 5% bioethanol by volume. In 2018, UK gasoline consisted of 4.6% of bioethanol on average.[20] The uplift of CO_2 emissions as a result is 3.2%, which is derived by multiplying the bioethanol/gasoline ratio (4.6/95.4) by the ratio of fuel CO_2 emissions (kg) per litre of bioethanol and gasoline (1.52/2.314).[23] NH_3/CO_2 is the average molar ratio from remote sensing measurements of gasoline passenger cars and M_{NH_3} and M_{CO_2} are the molar masses (kg mol^{-1}) of NH_3 and CO_2 respectively. The uncertainty of the NH_3 emission estimate is calculated by determining the 95% confidence interval of the molar NH_3/CO_2 ratio, and multiplying the upper and lower ratio limits

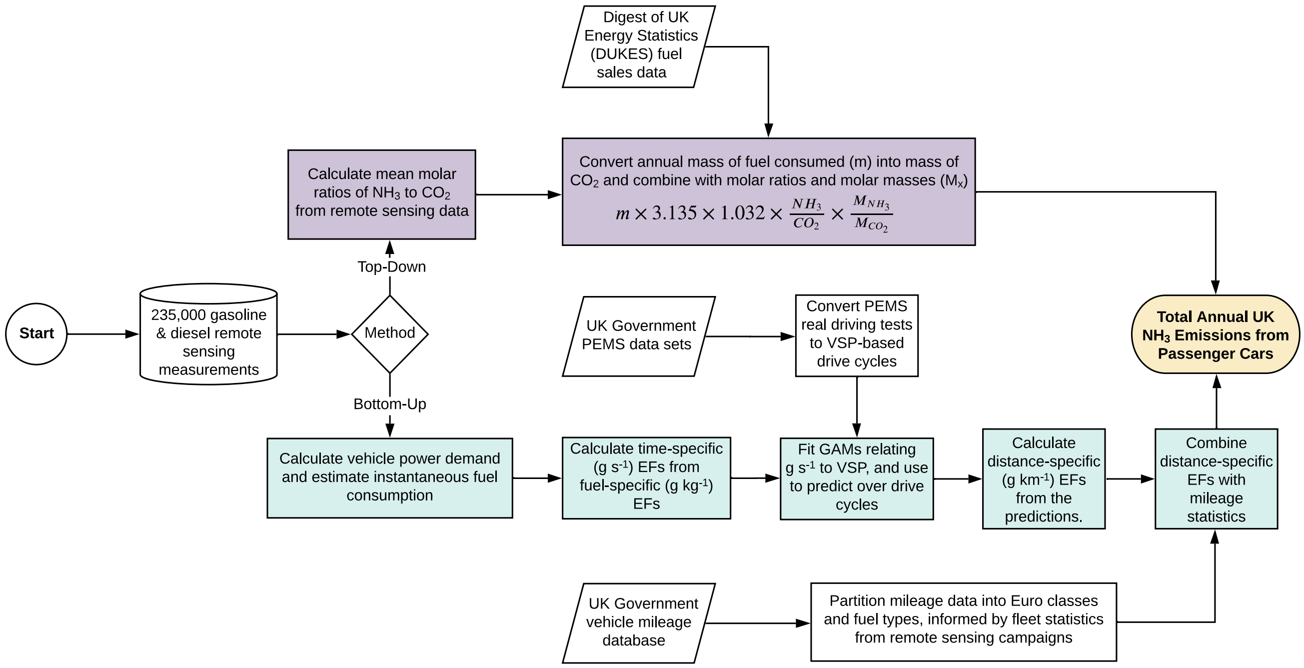

Figure 1: A flowchart showing the series of steps to calculate annual UK NH_3 emissions from remote sensing and external data sets, through both bottom-up (green) and top-down (purple) approaches. *EF* stands for Emission Factor and *GAM* for Generalised Additive Model.

by the remaining terms shown in Equation 1.

$$E_{NH_3} = m \times 3.135 \times 1.032 \times \frac{NH_3}{CO_2} \times \frac{M_{NH_3}}{M_{CO_2}} \quad (1)$$

Bottom-up estimate

A summary of the bottom-up estimates of total UK emissions of CO_2 and NH_3 is shown by the series of green shaded boxes in Figure 1 and starts with the 235,000 gasoline and diesel passenger car remote sensing measurements. A detailed vehicle-power based method is applied to express the emissions in $\mathrm{g\,km^{-1}}$ over a whole drive cycle. Comprehensive 1-Hz real driving data covering a wide range of conditions including urban, rural and motorway driving is used as the basis of calculating mean emissions for all vehicles over a wide range of driving conditions. Total UK emissions are then calculated using UK total vehicle km statistics for urban, rural and motorway driving. The methodology for calculating distance-specific emission factors from vehicle emission remote sensing data is described in detail in Davison et al.[24] but is briefly outlined here.

First, total engine power demand is determined using a physics-based approach, calculating the total power demand on the vehicle engine as the sum of the power to accelerate the vehicle, overcome both rolling and air resistance, climb the road gradient and power any auxiliary devices, with an appreciation for losses in the transmission. Vehicle Specific Power (VSP) in kW t^{-1} can then be calculated through division by vehicle mass. A vehicle power-based approach is used in preference to commonly used emission factor approaches that use average speed because of the much stronger relationship between vehicle power demand and emission (including CO_2 and air pollutants) compared with average speed, which we demonstrate later. A power-based approach also accounts for important driving conditions such as the strength and frequency of accelerations, vehicle idling and road gradient.

Vehicle mass was assumed to be the kerb weight (available from the the vehicle technical data) with an additional 150 kg to account for driver or passenger weight. As none of the road load or aerodynamic drag coefficients are known on an individual vehicle basis, generic values provided in Davison et al.[24] were used. A simple scheme for this approach is given in Equation 2, where P_x is the power demand from source x in kW, F_{trans} is a dimensionless adjustment factor to account for losses in the transmission, and M_v is the mass of the vehicle in tonnes.

$$VSP = \frac{(P_{accel} + P_{gradient} + P_{road} + P_{air}) \times F_{trans} + P_{auxiliary}}{M_v} \quad (2)$$

Fuel consumption is calculated based on the linear relationship with VSP derived from the Passenger Car and Heavy Duty Emissions Model (PHEM)[25]. As these parameters were based on Euro 5 and 6 vehicles, fuel consumption for Euro 3 and 4 vehicles were increased by 5% to approximate poorer fuel efficiency. With fuel consumption, it is straightforward to calculate a time-specific emission factor ($\mathrm{g\,s^{-1}}$) from a fuel-specific one ($\mathrm{g\,kg^{-1}}$) through multiplication by fuel consumption in $kg\ s^{-1}$.

Generalised Additive Models (GAMs) were then fit using the *mgcv* R package[26] to relate time-specific emission factors (in $\mathrm{g\,s^{-1}}$) to VSP in order to map remote sensing measurements to drive cycles. 1Hz Real Driving Emissions (RDE) tests from Portable Emission Measurement System (PEMS) measurements undertaken by the UK Department for Transport in 2016[27] were used. In total 58 RDE tests of lengths between 70.4 and 78.1 km were used — a total of 4243 km of real world driving. These tests aim to represent 'real driving' conditions and cover urban, rural and motorway driving conditions. The maximum VSP value across these drive cycles was 37.2 kW $\mathrm{t^{-1}}$ (corresponding to the 99.3rd percentile of remote sensing measurements). GAMs were fitted between 0 and 40 kW $\mathrm{t^{-1}}$, and emissions from negative VSPs were assumed to be zero. A small correction was made for gasoline hybrid cars, which accounted for 4.6% of the gasoline fleet in 2018 based on the remote sensing data. It was assumed that their fuel economy is 70% that of a standard gasoline-equivalent vehicle i.e. they emit 30% less CO_2 and ammonia than their conventional counterparts.

With 1 Hz modelled time-specific emissions, distance-specific emission factors ($\mathrm{g\,km^{-1}}$) can be calculated by summing all of the time-specific emission factors across the drive cycle and dividing by the total distance. The final distance-specific factor was taken to be the mean of all of the factors from each drive cycle. The outcome of this approach is an emission factor based on remote sensing measurements which reflects a wide range of real driving conditions. Distance-specific emission factors calculated for different combinations of fuel type and Euro standard can then be made to calculate a bottom-up estimation through multiplication with UK-wide mileage data. The associated uncertainty for the bottom-up NH_3 estimation is based on the 95% confidence interval of the fuel-based emission factors. The upper and lower limits can be expressed as a percentage of the mean, applied to the distance-based emission factors, and multiplied by the appropriate mileage data. Estimates of the total distance travelled by UK passenger cars per annum was obtained from a publicly available government database.[28]

The government data does not apportion the vehicle mileage into different fuel types or Euro classes, but adjustments for both of these factors can be made through information contained within the remote sensing data itself. Vehicle emission remote sensing is an effective way to capture not only the emissions of the fleet, but also its composition. For example, the data set used contains measurements of individual vehicle mileage, and indicates that the average diesel car has a mileage 1.32 times higher than the average gasoline car. The total mileage data was therefore split in a 1:1.32 ratio between gasoline and diesel respectively. However, the *number* of gasoline cars measured in the remote sensing data was 1.11 times greater than the number of diesel cars. Therefore, even though diesel cars drive further than gasoline cars overall, gasoline cars drive further in urban areas. As the remote sensing measurements were made predominantly in urban areas, this number of vehicles can be used to identify the ratio of *urban* mileage between the two fuel types. The urban mileage data was split in a 1.11:1 ratio between gasoline and diesel, and then the rural and motorway portions adjusted equally such that the total mileage for each fuel type was equal to the previously apportioned total annual mileage that includes urban, rural and motorway driving.

Apportionment into Euro classes was more straightforward. In 2018, 28.5% of passenger cars measured were Euro 6, 34.5% Euro 5, 23.4% Euro 4, 12.2% Euro 3 and 1.4% Euro 2. These proportions were used to partition the vehicle mileage for each of the combinations of fuel type and driving condition into Euro Classifications. The fully apportioned mileages are provided in Table S3.

Results and discussion

Total UK NH_3 estimates

In 2018, 11.1 Mt of gasoline was consumed by road vehicles in the UK.[29] This value is based on total annual fuel sales data provided in the Digest of UK Energy Statistics and is corrected for consumption by off-road vehicles and Crown Dependencies. Assuming that passenger cars account for 97% of total UK vehicular gasoline consumption,[17] this equates to 10.8 Mt of gasoline or 34.8 Mt of CO_2 for passenger cars (including an adjustment for CO_2 produced from bioethanol blended with gasoline). The average molar NH_3/CO_2 ratio for gasoline cars measured by RS was equal to $6.03\times10^{-4} \pm 7.6\times10^{-6}$. Using Equation 1, this leads to a top-down estimate of 8.1 ± 0.1 kt of NH_3 emitted from gasoline passenger cars in 2018.

At first glance, use of the average NH_3/CO_2 ratio from remote sensing measurements to derive UK annual NH_3 emissions from gasoline cars may seem like a gross oversimplification. However, this ratio is surprisingly comprehensive, as it originates from nearly 125,000 RS measurements of gasoline passenger cars and encompasses the broad range of vehicle physical characteristics and driving conditions encountered in the real world. For instance, the average ratio is already scaled according to the mix of Euro classes and vehicle manufacturers in the existing fleet. Furthermore, the ratio accounts for the amount of vehicle km driven and reflects the condition, or state of repair, of the vehicles on UK roads in 2018.

The results from the analysis of remote sensing data and the output from the emissions model show that in common with many other pollutants such as NO_x, NH_3 emissions are strongly influenced by driving conditions. Figure 2 shows how CO_2 and NH_3 vary with engine power, expressed as VSP. Analysis of variance testing on the fitted GAMs used for the bottom-up estimates confirmed that VSP was a significant predictor ($P < 0.05$) for CO_2 and NH_3 $\mathrm{g\,s^{-1}}$ in all cases for Euro 2–6 gasoline and Euro 6 diesel passenger cars. In the case of CO_2, there is a close to linear relationship between VSP and emission, which shows the benefit of expressing emissions as a function of vehicle power demand rather than other metrics such as vehicle speed. NH_3 emissions also have a strong relationship with VSP, with increasing emissions for older Euro standard vehicles.

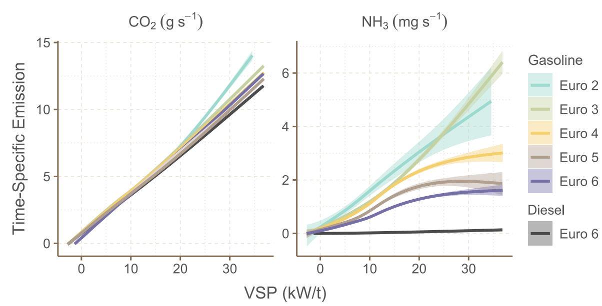

Figure 2: Generalised Additive Models (GAMs) relating passenger car CO_2 $\mathrm{g\,s^{-1}}$ and NH_3 $\mathrm{mg\,s^{-1}}$ to VSP, labelled by Euro classification and fuel type. The shading shows the standard error of the GAM fit.

The calculated distance-specific CO_2 and NH_3 emissions factors for UK passenger cars are provided in Figure 3. The $\mathrm{g\,kg^{-1}}$ and $\mathrm{g\,km^{-1}}$ emission factors and their associated uncertainties, categorised by fuel type and Euro classification, can also be found in Tables S4 and S5. NH_3 $\mathrm{mg\,km^{-1}}$ values are seen to decrease with increasing Euro status in the case of the gasoline passenger vehicles. The Euro 6 diesel $\mathrm{mg\,km^{-1}}$ values are roughly thirty times lower than the equivalent Euro 6 gasoline values.

Multiplying each of the urban, rural and mo-

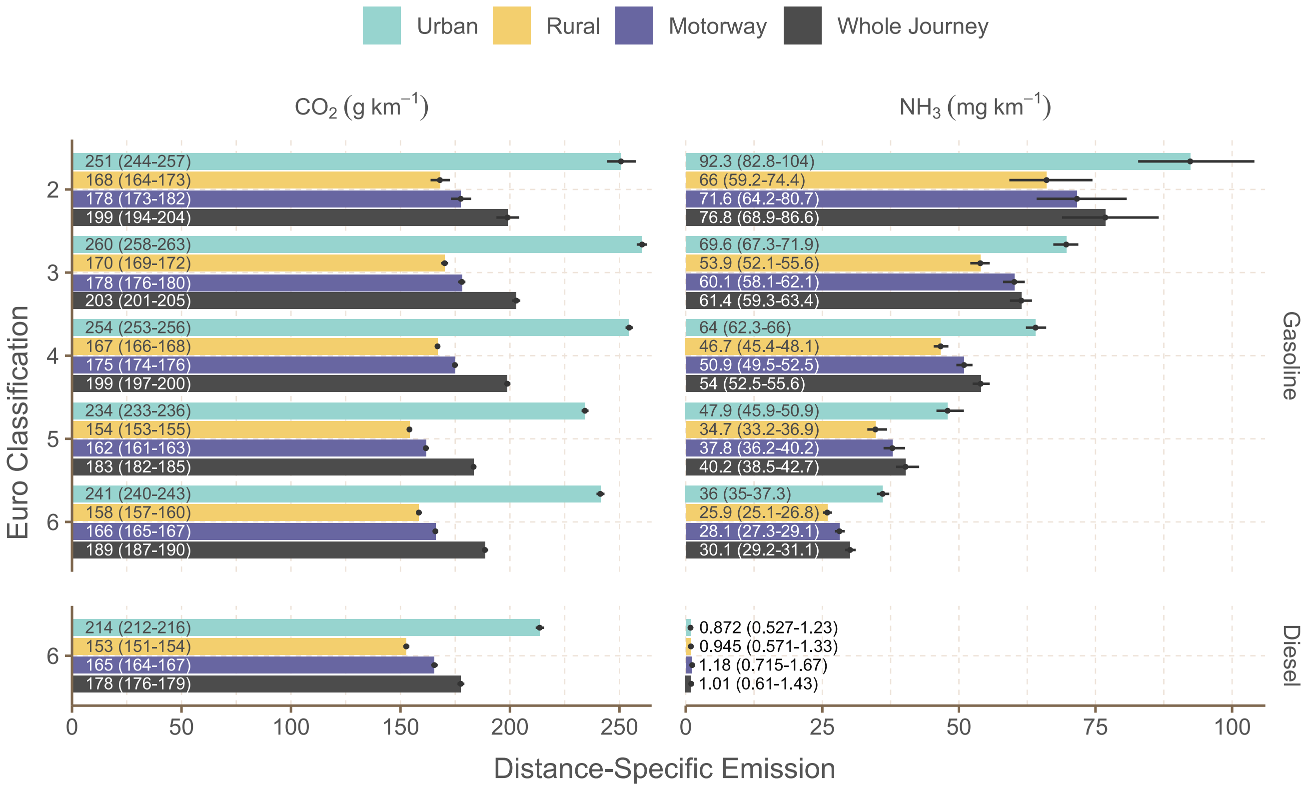

Figure 3: Distance-specific emission factors for CO_2 and NH_3 emissions of gasoline and diesel cars, disaggregated by Euro classification and driving condition. Factors are determined from the predictions of GAMs relating $g\,s^{-1}$ emission factors to VSP over a VSP-based drive cycle taken from a real driving emissions test.

torway distance-specific emission factors by the mileages shown in Table S3 and calculating the total emission from the sum of these gives a bottom-up estimate of 35.2 ± 0.3 Mt of CO_2 and 7.8 ± 0.3 kt of NH_3 in 2018 for gasoline passenger cars. The bottom-up estimate of NH_3 emissions compares very well with the top-down estimate of 8.1 ± 0.1 kt. Importantly the 35.2 Mt CO_2 from the bottom-up approach is in excellent agreement with the top-down of 34.8 Mt, which is derived from total UK gasoline fuel sales and is a quantity known to high accuracy. Given the number of steps involved in the bottom-up calculations, the agreement with the top-down approach is very encouraging and provides some confidence that the method achieves fuel / carbon balance at a national level. It also provides confidence the estimated emissions of NH_3 are not biased because the total fuel consumed differs from the national total.

The remote sensing measurements suggest diesel passenger cars only make a minor contribution to total passenger car emissions of NH_3. Pre-Euro 6 diesel cars effectively have zero NH_3 emissions. The bottom-up estimate for the Euro 6 diesel passenger cars is 11.6 ± 0.1 Mt of CO_2 and 65 ± 30 t of NH_3 (about 0.8% of the total NH_3 emissions of the gasoline passenger cars). The contribution from diesel passenger cars is dominated by SCR-equipped vehicles with only a minor contribution from vehicles using a Lean NO_x Trap (LNT).

Comparison with the UK national inventory

The comprehensive measurements and analysis that underpin the current work considerably strengthen the evidence base of NH_3 emissions from passenger cars. The NAEI calculates NH_3 emissions for the UK using emission factors for NH_3 from COPERT 5, a software program used for the calculation of air pollutant emissions from road transport. The emission factors are based on the recommendation of the EMEP/EEA Emission Inventory Guidebook. For gasoline cars, the COPERT emission factors for NH_3 are provided for different Euro standards and driving conditions (urban, rural and highway), with adjustment factors that take into account vehicle mileage and fuel sulphur content. The emission factors are derived from reviews of literature data collected from studies around the world undertaken in 2005 and 2014.[30,31]

However, the evidence from literature is limited and the emission factors developed do not necessarily represent the current UK fleet. For Euro 5 and 6 gasoline passenger cars, the derived emission factors are based on chassis dynamometer test cycle measurements from fewer than 30 vehicles, for which limited information on aftertreatment technology is provided. The data used to derive NH_3 emission factors for Euro 5 and 6 diesel vehicles is sparse and is based on measurements from 1 passenger car and 2 heavy duty vehicles. As the majority of the studies were carried out in the US, several assumptions are needed to convert US vehicle technologies into equivalent European based emission standards. The 2014 review of literature data highlights the need for more relevant testing, especially to assess the emissions for different driving conditions (urban, rural and motorway) and the impact of mileage on NH_3 emissions.

Overall, we estimate that NH_3 emissions from gasoline passenger cars are a factor of 2.6 times higher than is reported in the NAEI for total UK emissions (7.8 ± 0.3 kt yr^{-1} compared with 3.0 ± 1.7 kt yr^{-1} for the national inventory). However, as shown in Figure 3, emissions of NH_3 are higher under urban-type driving conditions than rural or motorway driving. We estimate that approximately 52% of the total NH_3 emissions from gasoline passenger cars can be attributed to urban areas (the remaining 48% is allocated to motorways and rural areas). The 52% value for the urban component compares with 9% estimated by the NAEI. These results therefore suggest that in urban areas, emissions of NH_3 from road vehicles are underestimated by a factor of 17.

Implications

This study gives us a better insight into the absolute value of NH_3 estimate and the fraction of vehicle NH_3 in terms of the UK total, which is important in terms of the air quality implications. The main findings that emissions of NH_3 are considerably underestimated from road vehicles in the UK likely also applies to most other European countries that use COPERT emission factors as a basis for national inventory development. Another common approach for emission factor calculation is the HBEFA approach (Hand Book on Emission Factors for Road Transport).[32] HBEFA however bases its NH_3 emission factors on COPERT and will therefore likely also underestimate NH_3 emissions from gasoline passenger cars. It has however been recognised that emissions of NH_3 may be underestimated. In the Netherlands for example, a review of emission factors for NH_3 from passenger cars and LCVs resulted in correction factors being developed that increased emissions, in part based on earlier vehicle emission remote sensing measurements.[33,34]

While the revised estimates of total passenger car emissions of NH_3 are more than double that in the NAEI, the road transport contribution to total UK NH_3 is still small. For 2018, the NAEI suggests that road transport NH_3 contributed only 1.6% of total UK emissions, whereas the revised estimates in the current work would suggest gasoline passenger cars contribute 2.8%. However, as previously discussed, an important characteristic of NH_3 emissions from road vehicles is that they are co-emitted with NO_x, both from road vehicles and other sources such as domestic and commercial natural gas combustion. Furthermore, the revised NH_3 emission estimates from road vehicles for urban areas are about a factor of 17 higher than the UK national inventory, suggesting that for the inventory both total NH_3 emissions — and importantly, the amount of NH_3 released in urban areas is significantly underestimated. Such a considerable increase in the absolute emissions of NH_3 in urban areas could have important consequences from an atmospheric chemistry perspective providing a more efficient route to $PM_{2.5}$ formation.

The quantification of significantly increased urban NH_3 on $PM_{2.5}$ formation would however require detailed air quality modelling.

Currently in Europe, work is being undertaken to develop what will become Euro 7/VII emissions regulations.[35] This work is considering the development of emission limits for currently unregulated emissions including NH_3, nitrous oxide (N_2O), methane and formaldehyde. However, the emissions data for these species (especially under real driving conditions) is considerably more limited than is the case for NO_x, CO and total hydrocarbons. The development of the RDE regulations where on-road testing is conducted using PEMS in addition to laboratory measurements should mitigate against any discrepancies that have historically been important between laboratory and on-road emissions performance. However, it will be important for the development of any Euro 7 legislation that specific attention is paid to emissions under urban driving conditions to ensure effective performance. The emission factors developed and used in the current work for NH_3 are therefore timely and valuable.

Another important factor is the relative share of gasoline and diesel fuel use in the light duty vehicle fleet. The dieselgate[36] scandal in September 2015 has strongly affected the sales of gasoline and diesel cars in the UK and Europe, with a considerable increase in the sale of gasoline vehicles at the expense of diesel. In 2015, there was an even split between gasoline and diesel new passenger car registrations. However, by the first quarter of 2020 only 22% of new vehicle passenger cars were diesel.[37] This trend has some potentially important implications for NH_3 emissions given the dominance of emissions from gasoline vehicles. The increasing relative share of gasoline vehicles in the fleet will tend to further increase total UK emissions of NH_3. Moreover, these vehicles will remain in the fleet for many years to come, and as they age, NH_3 emissions will likely increase further.

Acknowledgement The authors would like to thank Dr Gary Bishop from the University of Denver for use of the FEAT instrument. Funding from the International Council on Clean Transportation (ICCT) to support some of the London measurements is gratefully acknowledged. Jack Davison was supported by NERC grant NE/S012044/1. We would like to thank Adam Vaughan, Stuart Young and Will Drysdale from the University of York for the collection of data using the FEAT instrument. Ricardo Energy & Environment's remote sensing field team (Ben Fowler, Tom Green, Les Phelps, Sam Copsey, Paraic Marry, Sion Carpenter and Susannah Telfer) are thanked for collecting data using the Opus RSD 5000.

Supporting Information

Table S1: Specifications of the gas cylinders used for calibration of the FEAT and RSD 5000 (BOC UK & Ireland). Table S2: Site location information for the UK remote sensing surveys. Table S3: Annual UK passenger car mileage in billions of kilometers. Table S4: Fuel specific ($g\,kg^{-1}$) emission factors for CO_2 and NH_3. Table S5: Fuel specific ($g\,km^{-1}$ and $mg\,km^{-1}$) emission factors for CO_2 and NH_3.

References

(1) Nowak, J. B.; Neuman, J. A.; Bahreini, R.; Brock, C. A.; Middlebrook, A. M.; Wollny, A. G.; Holloway, J. S.; Peischl, J.; Ryerson, T. B.; Fehsenfeld, F. C. Airborne observations of ammonia and ammonium nitrate formation over Houston, Texas. *Journal of Geophysical Research Atmospheres* **2010**, *115*, D22304.

(2) Asman, W. A.; Sutton, M. A.; Schjørring, J. K. Ammonia: Emission, atmospheric transport and deposition. *New Phytologist* **1998**, *139*, 27–48.

(3) Department for environment food and rural affairs, *Clean Air Strategy 2019*; 2019.

(4) National Atmospheric Emissions Inventory, Pollutant Information: Ammonia. 2018; https://naei.beis.gov.uk/overview/pollutants?pollutant_id=21.

(5) Wang, M.; Kong, W.; Marten, R.; He, X. C.; Chen, D.; Pfeifer, J.; Heitto, A.; Kontkanen, J.; Dada, L.; Kürten, A.; Yli-Juuti, T.; Manninen, H. E.; Amanatidis, S.; Amorim, A.; Baalbaki, R.; Baccarini, A.; Bell, D. M.; Bertozzi, B.; Bräkling, S.; Brilke, S.; Murillo, L. C.; Chiu, R.; Chu, B.; De Menezes, L. P.; Duplissy, J.; Finkenzeller, H.; Carracedo, L. G.; Granzin, M.; Guida, R.; Hansel, A.; Hofbauer, V.; Krechmer, J.; Lehtipalo, K.; Lamkaddam, H.; Lampimäki, M.; Lee, C. P.; Makhmutov, V.; Marie, G.; Mathot, S.; Mauldin, R. L.; Mentler, B.; Müller, T.; Onnela, A.; Partoll, E.; Petäjä, T.; Philippov, M.; Pospisilova, V.; Ranjithkumar, A.; Rissanen, M.; Rörup, B.; Scholz, W.; Shen, J.; Simon, M.; Sipilä, M.; Steiner, G.; Stolzenburg, D.; Tham, Y. J.; Tomé, A.; Wagner, A. C.; Wang, D. S.; Wang, Y.; Weber, S. K.; Winkler, P. M.; Wlasits, P. J.; Wu, Y.; Xiao, M.; Ye, Q.; Zauner-Wieczorek, M.; Zhou, X.; Volkamer, R.; Riipinen, I.; Dommen, J.; Curtius, J.; Baltensperger, U.; Kulmala, M.; Worsnop, D. R.; Kirkby, J.; Seinfeld, J. H.; El-Haddad, I.; Flagan, R. C.; Donahue, N. M. Rapid growth of new atmospheric particles by nitric acid and ammonia condensation. *Nature* **2020**, *581*, 184 – 189.

(6) Pan, Y.; Tian, S.; Liu, D.; Fang, Y.; Zhu, X.; Zhang, Q.; Zheng, B.; Michalski, G.; Wang, Y. Fossil Fuel Combustion-Related Emissions Dominate Atmospheric Ammonia Sources during Severe Haze Episodes: Evidence from ^{15}N-Stable Isotope in Size-Resolved Aerosol Ammonium. *Environmental Science and Technology* **2016**, *50*, 8049–8056.

(7) Ntziachristos, L.; Samaras, Z.; Kouridis, C.; Samaras, C.; Hassel, D.; Mellios, G.; McCrae, I.; Hickman, J.; Zierock, K.-H.; Keller, M.; Rexeis, M.; Andre, M.; Winther, M.; Pastramas, N.; Gorissen, N.; Boulter, P.; Katsis, P.; Joumard, R.; Rijkeboer, R.; Geivanidis, S.; Hausberger, S. EMEP/EEA air pollutant emission inventory guidebook 2019, 1.A.3.b.i-iv Road transport. 2019.

(8) Suarez-Bertoa, R.; Astorga, C. Isocyanic acid and ammonia in vehicle emissions. *Transportation Research Part D: Transport and Environment* **2016**, *49*, 259–270.

(9) Whittington, B. I.; Jiang, C. J.; Trimm, D. L. Vehicle exhaust catalysis: I. The relative importance of catalytic oxidation, steam reforming and water-gas shift reactions. *Catalysis Today* **1995**, *26*, 41–45.

(10) Barbier, J.; Duprez, D. Steam effects in three-way catalysis. 1994.

(11) European Commission, Commission regulation (EU) No 582/2011 of 25 May 2011 implementing and amending Regulation (EC) No 595/2009 of the European Parliament and of the Council with respect to emissions from heavy duty vehicles (Euro VI) and amending Annexes I and III to Directive 2007/46/EC of the European Parliament and of the Council. 2011.

(12) Bishop, G. A.; Stedman, D. H. Reactive Nitrogen Species Emission Trends in Three Light-/Medium-Duty United States Fleets. *Environmental Science and Technology* **2015**, *49*, 11234 – 11240.

(13) Meng, W.; Zhong, Q.; Yun, X.; Zhu, X.; Huang, T.; Shen, H.; Chen, Y.; Chen, H.; Zhou, F.; Liu, J.; Wang, X.; Zeng, E. Y.; Tao, S. Improvement of a Global High-Resolution Ammonia Emission Inventory for Combustion and Industrial Sources with New Data from the Residential and Transportation Sectors. *Environmental Science and Technology* **2017**, *51*, 2821–2829.

(14) Sun, K.; Tao, L.; Miller, D. J.; Pan, D.; Golston, L. M.; Zondlo, M. A.; Griffin, R. J.; Wallace, H. W.; Leong, Y. J.; Yang, M. M.; Zhang, Y.; Mauzerall, D. L.; Zhu, T. Vehicle Emissions as an Important Urban Ammonia Source in the United States and China. *Environmental Science and Technology* **2017**, *51*, 2472–2481.

(15) National Atmospheric Emissions Inventory, UK emissions data selector: Ammonia. 2018; https://naei.beis.gov.uk/data/data-selector?view=air-pollutants.

(16) Burgard, D. A.; Bishop, G. A.; Stadtmuller, R. S.; Dalton, T. R.; Stedman, D. H. Spectroscopy Applied to On-Road Mobile Source Emissions. *Applied Spectroscopy* **2006**, *60*, 135A–148A.

(17) Department for Transport, Petroleum consumption by transport mode and fuel type: United Kingdom (ENV0101). 2020; https://www.gov.uk/government/statistical-data-sets/energy-and-environment-data-tables-env.

(18) Trombetti, M.; Thunis, P.; Bessagnet, B.; Clappier, A.; Couvidat, F.; Guevara, M.; Kuenen, J.; López-Aparicio, S. Spatial inter-comparison of Top-down emission inventories in European urban areas. *Atmospheric Environment* **2018**, *173*, 142 – 156.

(19) Pallavidino, L.; Prandi, R.; Bertello, A.; Bracco, E.; Pavone, F. Compilation of a road transport emission inventory for the Province of Turin: Advantages and key factors of a bottom-up approach. *Atmospheric Pollution Research* **2014**, *5*, 648 – 655.

(20) Department for Business, Energy & Industrial Strategy, Digest of UK Energy Statistics (DUKES). 2020; https://www.gov.uk/government/collections/digest-of-uk-energy-statistics-dukes.

(21) Ricardo Energy & Environment, Methodology for the UK's Road Transport Emissions Inventory, Version for the 2016 National Atmospheric Emissions Inventory. 2018; https://uk-air.defra.gov.uk/assets/documents/reports/cat07/1804121004_Road_transport_emissions_methodology_report_2018_v1.1.pdf.

(22) United Kingdom Petroleum Industry Association, Communication on properties of UK fuels. 2004.

(23) Department for Business, Energy & Industrial Strategy, Greenhouse gas reporting: conversion factors 2020. 2020; https://www.gov.uk/government/publications/greenhouse-gas-reporting-conversion-factors

(24) Davison, J.; Bernard, Y.; Borken-Kleefeld, J.; Farren, N. J.; Hausberger, S.; Sjödin, Å.; Tate, J. E.; Vaughan, A. R.; Carslaw, D. C. Distance-based emission factors from vehicle emission remote sensing measurements. *Science of the Total Environment* **2020**, *739*, 139688.

(25) Hausberger, S. *Simulation of Real World Vehicle Exhaust Emissions*; Technische Universität Graz: Austria, 2003; Vol. 82; VKM-THD Mitteilung.

(26) Wood, S. *Generalized Additive Models: An Introduction with R*, 2nd ed.; Chapman and Hall/CRC, 2017.

(27) Department for Transport, Vehicle Emissions Testing Programme. 2016; https://www.gov.uk/government/publications/vehicle-emissions-testing-programme-conclusions.

(28) Department for Transport, Quarterly traffic estimates (TRA25). 2020; data retrieved from TRA2506, https://www.gov.uk/government/statistical-data-sets/tra25-quarterly-estimates.

(29) Richmond, B.; Misra, A.; Brown, P.; Karagianni, E.; Murrells, T.; Pang, Y.; Passant, N.; Pepler, A.; Stewart, R.; Thistlethwaite, G.; Turtle, L.; Wakeling, D.; Walker, C.; Wiltshire, J.; Hobson, M.; Gibbs, M.; Misselbrook, T.; Dragosits, U.; Tomlinson, S. UK Informative Inventory Report (1990 to 2018). 2020; https://uk-air.defra.gov.uk/assets/documents/reports/cat07/2003131327_GB_IIR_2020_v1.0.pdf.

(30) Papathanasiou, L.; Tzirgas, S. N2O and NH3 emission factors from road vehicles. LAT/AUTh report 0507, Thessaloniki, Greece. 2005.

(31) Pastramas, N.; Samaras, C.; Mellios, G.; Ntziachristos, L. Update of the Air Emissions Inventory Guidebook - Road Transport 2014 Update. EMISIA SA Report No. 14.RE.011.V1. 2014.

(32) Matzer, C.; Weller, K.; Dippold, M.; Lipp, S.; Röck, M.; Rexeis, M.; Hausberger, S. Update of emission factors for HBEFA Version 4.1; Final report, I-05/19/CM EM-I-16/26/679 from 09.09.2019, TU Graz. 2019.

(33) Stelwagen, I. U.; Ligterink, N. E. NH_3 emission factors for road transport. TNO 2015 R11005. 2015; http://www.emissieregistratie.nl/erpubliek/documenten/Lucht%20(Air)/Verkeer%20en%20Vervoer%20(Transport)/Wegverkeer/TNO%20(2015)%20NH3%20Emission%20Factors%20for%20road%20transport.pdf (last accessed 18 August 2020).

(34) Carslaw, D. C.; Rhys-Tyler, G. New insights from comprehensive on-road measurements of NO_x, NO_2 and NH_3 from vehicle emission remote sensing in London, UK. *Atmospheric Environment* **2013**, *81*, 339 – 347.

(35) AGVES, Study on post-EURO 6/VI emission standards in Europe. Presentation to the Advisory Group on Vehicle Emission Standards (AGVES) Brussels, October 18, 2019. 2019; https://circabc.europa.eu/sd/a/a108e064-c487-4bf6-bb46-7faac76f8205/Post-EURO%206%20WT2.2_AGVES_2019_10_18%20V4.pdf (last accessed 18 August 2020).

(36) Thompson, G. J.; Carder, D. K.; Besch, M. C.; Thiruvengadam, A.; Kappanna, H. K. In-Use Emissions Testing of Light-Duty Diesel Vehicles in the United States. 2014.

(37) Department for Transport, VEH0253: Cars registered for the first time by propulsion and fuel type: Great Britain and United Kingdom. 2020; https://www.gov.uk/government/statistical-data-sets/veh02-licensed-cars.

Graphical TOC Entry