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Strong Temperature Dependence for Light-Duty Diesel Vehicle NO_x Emissions

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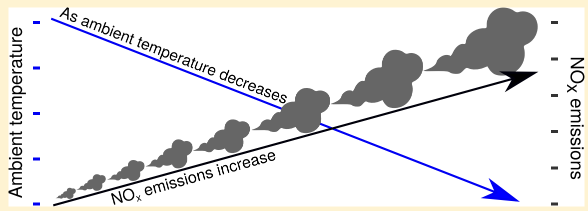
Supporting Information

ABSTRACT: Diesel-powered road vehicles are important sources for nitrogen oxide (NO_x) emissions, and the European passenger fleet is highly dieselised, which has resulted in many European roadside environments being noncompliant with legal air quality standards for nitrogen dioxide (NO_2). On the basis of vehicle emission remote sensing data for 300000 light-duty vehicles across the United Kingdom, light-duty diesel NO_x emissions were found to be highly dependent on ambient temperature with low temperatures resulting in higher NO_x emissions, i.e., a "low temperature NO_x emission penalty" was identified. This feature was not observed for gasoline-powered vehicles. Older Euro 3 to 5 diesel vehicles emitted NO_x similarly, but vehicles compliant with the latest Euro 6 emission standard emitted less NO_x than older vehicles and demonstrated less of an ambient temperature dependence. This ambient temperature dependence is overlooked in current emission inventories but is of importance from an air quality perspective. Owing to Europe's climate, a predicted average of 38% more NO_x emissions have burdened Europe when compared to temperatures encountered in laboratory test cycles. However, owing to the progressive elimination of vehicles demonstrating the most severe low temperature NO_x penalty, light-duty diesel NO_x emissions are likely to decrease more rapidly throughout Europe than currently thought.



INTRODUCTION

European roadside environments remain polluted with nitrogen oxides (NO_x), and legal standards for ambient concentrations of nitrogen dioxide (NO_2), the regulated component of NO_x, are widely exceeded throughout Europe.[1,2] The lack of compliance to the legal standards has resulted in a range of potentially disruptive air quality management and intervention actions in an attempt to accelerate the reduction in concentrations to below limit values such as banning of private vehicles, low emission zones, and the introduction of progressively stringent emission standards.[3−6] The principal challenge is meeting the annual mean NO_2 of 40 μg m^{-3} close to roads across European urban environments.

The recent focus for vehicle emissions research has been the quantification of the discrepancy between type approval and real-world emissions performance of diesel passenger cars.[7] Much of this focus stems from the Volkswagen diesel emission scandal, also known as "dieselgate" in late September 2015.[8−10] On-road NO_x emissions from diesel vehicles have been found to be much higher than thought prediesel emission scandal, and many Euro 6 vehicles have been found to have inadequate NO_x control when operated in real-world situations.[11−15] It has been known for many years that type approval laboratory-based emission measurements are lower than on-road measurements, and for this reason, emission factor databases such as COPERT do not use type approval emission measurements.[16]

There are a myriad reasons for discrepancies between laboratory and on-road emissions. However, there is a growing body of evidence from laboratory testing that NO_x emissions from vehicles are highly dependent on ambient temperature.[17−22] Specifically, NO_x emissions are suggested to be higher during temperatures below ≈15 °C for diesel-powered vehicles with Euro emission standards of 3 to 5 (vehicles manufactured between approximately 2000 and 2015).[17] There is also evidence for the two primary NO_x after-treatment technologies employed for Euro 6 diesel compliance: lean NO_x traps (LNT or NO_x absorbers) and selective catalytic reduction (SCR) behave differently in real world situations.[23,24] This temperature dependence needs to be thought of as independent of cold start emissions where internal combustion engines require fuel−air ratio enrichment and other strategies while the engine, lubricants, and catalytic devices reach operating temperatures which all result in greater emissions of pollutants for a short period of time.[25,26]

Type approval emission testing in Europe is performed between 20 and 30 °C.[14] While the standardization of the test cycle is a benefit from the perspective of ensuring consistent test conditions, it does not necessarily reflect prevailing ambient conditions across Europe or in many other regions

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of the world. The particular temperature range used for test cycles is a pragmatic choice because these temperatures are easily achieved without excessive heating or cooling requirements when vehicles are operated in laboratory settings. However, some emission factor databases such as the Handbook Emission Factors for Road Transport (HBEFA) have introduced preliminary NO_x emission correction factors, which will be revised when more data become available.[19] It is important to note that although effective NO_x control has proven to be a challenge for diesel-powered passenger vehicle manufacturers,[27,28] the technology does exist to comply with current NO_x emission limits.[14]

Despite the focus on temperature, humidity is also an important atmospheric parameter to consider for diesel and gasoline NO_x emissions.[29] High humidity within a combustion chamber offers a physical mechanism for reducing NO_x formation due to the reduction of peak flame front temperature and an increase of combustion duration.[30,31] The amount of water vapor contained in inlet air is the driver of this effect, and therefore absolute humidity (AH) is the measure used rather than relative humidity (RH). The United States MOtor Vehicle Emission Simulator (MOVES) takes humidity (and temperature) effects into account and adjusts emissions to reference conditions.[32,33] However, such adjustments do not necessarily represent real-world vehicle operation where it is important to understand such influences and their potential to affect ambient pollutant concentrations.

Low ambient temperatures are important from the perspective of the dispersion of air pollutants. During periods of low temperatures, concentrations of locally emitted, ground-level sources tend to be at their highest due to less effective dispersion resulting from stable atmospheric conditions and a lack of wind.[34] Low temperatures also result in increased emissions of many atmospheric pollutants due to increases in anthropogenic energy demands which are generally met by combustion activities.[35] When these meteorological conditions persist for several days, often an air pollution episode is experienced. The combination of meteorological factors and increased emissions due to some activities such as space heating are well documented.[36,37] However, it remains difficult to understand the relative contributions of increased source emissions and meteorological influences on the concentrations of atmospheric pollutants such as NO_x. In the case of vehicle emissions, understanding the effect of ambient temperature is of primary importance given the impact that vehicle emissions have on the exposure of urban populations.

The implications for increased NO_x emissions at lower temperatures for roadside European air quality are poorly understood but are of importance. Currently, emission inventories such as the United Kingdom National Atmospheric Emissions Inventory (NAEI) do not account for a dependence between vehicular emissions and ambient temperature, which would result in less than optimal modeling of emissions and ambient concentrations. This situation is especially relevant for cold periods where the combination of poor dispersion and increased emissions could combine, resulting in more extreme poor air quality episodes than would be expected without taking into account the temperature effect. Such an effect will be unevenly distributed throughout Europe because of the range of climatic conditions experienced. Countries or cities located in cooler areas would have been burdened with increased NO_x emissions once diesel vehicles began to significantly penetrate the European passenger vehicle fleet, beginning in the mid-1990s assuming similar diesel uptake rates. This effect would also perturb the estimations of health burdens resulting from NO_x emissions, which has been extensively considered after the diesel emission scandal.[38−40]

The effect of ambient temperature on vehicle emissions is difficult to robustly quantify using chassis dynamometers (rolling roads) or portable emission measurements systems (PEMS) because it is only practical to test a relatively small number of vehicles.[17,41] In principle, using a remote sensing technique is attractive because it offers the potential to measure far greater numbers of vehicles under a wide range of driving conditions. The remote sensing approach also offers the benefit of real-world measurements, driven by their drivers with very little chance of the vehicle detecting that it is undergoing an emissions test.[20] The remote sensing technique captures vehicles under a range of vehicle operating conditions. However, it is not possible to establish the specific operating conditions of individual vehicles such as whether they have hot or cold engines and whether vehicle aftertreatment technologies such as SCR are operating at optimum temperature. Instead, by measuring at a wide range of locations (26 in the current case) under a wide range of driving conditions, the emission characteristics of typical urban driving are quantified.

The primary objective of this work is to investigate and quantify the influence of ambient temperature on light-duty vehicle NO_x emissions using on-road remote sensing observations from field campaigns conducted between 2017 and 2018. A further objective is to consider the implications of any temperature dependence of vehicular NO_x emissions on roadside air quality in Europe.

■ MATERIALS AND METHODS

Measurement Locations. Remote sensing of on-road vehicle emissions was conducted in ten regions and 26 sites throughout the United Kingdom (England, Scotland, and Wales) in 2017 and 2018 (Table 1 and Figure 1). All sites were suburban in nature with the exception of the A10/M25 Junction site which was a motorway on-ramp (a slip road). The ambient temperature range experienced across these field campaigns was 0.5−24.8 °C with the greatest number of vehicle captures being conducted in the midteens (Figure S1). Such temperatures are typical for most of the United Kingdom, but there was some bias toward warmer temperatures due to more favorable field conditions. All field campaigns were conducted during Mondays and Fridays and in daylight hours (06:00−18:00), with some periods where monitoring stopped due to rain. The mean vehicle speed for valid captures was 36.1km h^{-1} with a standard deviation of 9.1km h^{-1}.

Instrumentation. The equipment used to capture on-road vehicle emissions included three main components: a spectroscopic remote sensing device (RSD), speed bar lasers, and a video camera. A RSD was set up perpendicular to the flow direction of a single lane of traffic, such that the light source is directed through individual vehicle exhaust plumes. Measurements were obtained using two RS instruments: the fuel efficiency automobile test (FEAT) research instrument supplied by the University of Denver and an Opus RSD 5000.[42,43] The development and operation of the FEAT has been described elsewhere,[44−46] and an intercomparison of the two RSD instruments conducted in the United Kingdom (Leeds, England) has been previously reported.[47]

The Denver FEAT instrument consists of a nondispersive infrared (NDIR) system and a dispersive ultraviolet system.

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Table 1. Information about the 26 Monitoring Sites Where on-Road Remote Sensing Took Place in 2017 and 2018[a]

Site	Road ref.	Region	Lat.	Long.	Elevation (m)
Queen Margaret Drive		Glasgow	55.88	−4.29	34
Clydeside Expressway	A814	Glasgow	55.87	−4.32	9
Nelson Mandela Place		Glasgow	55.86	−4.25	16
East Mains Road	B783	South Lanarkshire	55.77	−4.17	162
Clifton Moor Gate		York	53.99	−1.09	16
Poppleton Roundabout	A59	York	53.97	−1.14	21
University of York University Road		York	53.95	−1.05	26
Barton Dock Road	B511	Manchester	53.47	−2.35	26
Stafford Street	A601	Derby	52.92	−1.48	53
Mercian Way	A601	Derby	52.92	−1.48	53
St. Quentin		Shropshire	52.67	−2.44	143
Headington	A420	Oxfordshire	51.75	−1.24	64
A10/M25 Junction	M25	London	51.68	−0.05	39
Hafod-yr-ynys Road	A472	Caerphilly	51.68	−3.12	211
Rowstock	A4185	Oxfordshire	51.60	−1.31	98
Harwell Campus out-bound		Oxfordshire	51.58	−1.31	122
Harwell Campus in-bound		Oxfordshire	51.58	−1.31	122
West End Road	A4180	London	51.57	−0.42	47
Greenford Road	A4127	London	51.52	−0.35	6
Stockley Road link	A408	London	51.51	−0.45	39
Dawley Road		London	51.50	−0.43	32
Heston Road	A3005	London	51.49	−0.37	29
Woolwich Common	A205	London	51.48	0.06	31
Putney Hill	A219	London	51.46	−0.22	37
Christchurch Road	A205	London	51.44	−0.11	59
Callington Road	A4174	Bristol	51.43	−2.56	34

[a]For locations of the regions, see Figure 5.

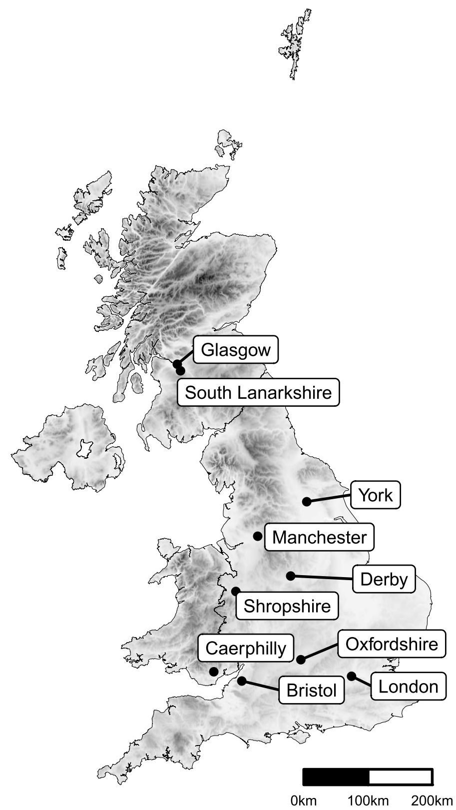

Figure 1. Ten regions where on-road remote sensing sessions were conducted in the United Kingdom during 2017 and 2018.

The system contains a dual-element light source (silicon carbide gas drier igniter and a xenon arc lamp) and a detector unit. The attenuation of light as it passes through the exhaust plume provides a measure of the incremental concentrations of various pollutants of interest compared to ambient background levels. Carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HCs), and a background reference are obtained using nondispersive infrared (IR) spectroscopy, while UV spectrometers are used to determine ammonia (NH_3), nitric oxide (NO), and NO_2. All species are quantified as a ratio to CO_2 to account for variation in the density, position, and path length of the vehicle exhaust plume. Unlike the Denver FEAT instrument, the Opus RSD 5000 does not have a dedicated spectrometer for NO_2.[47] Mean NO and NO_2 for the two instruments by the air temperatures encountered while capturing vehicles are displayed in Figure S2.

The RS instruments were calibrated in situ every few hours to account for changes in instrument performance, instrument path length, and ambient CO_2 concentrations (caused by variation in local CO_2 sources and atmospheric pressure). This was achieved using certified calibration gas cylinders containing known ratios and concentrations of gases. The cylinders used for these calibrations were different for the two instruments, and their details can be found in Table S1. Small amounts of gas from the cylinders were released into the instruments' path to allow for a comparison of the measured ratios from the instruments to those certified by the gas cylinder manufacturer. The use of speed bar lasers alongside the RSD provided a measurement of both vehicle speed and acceleration for each passing vehicle. These variables, combined with road gradient and vehicle mass, were used to determine engine load for the vehicle at the instant it drives through the RSD path. Ratios of pollutants to CO_2 were used to derive fuel-specific emission factors in g kg^{-1}. The calculations used for these transformations can be found elsewhere.[44,48]

A video camera was used to photograph the vehicle registration plate of each vehicle passing the RSD. The registration plate images were digitized and sent to a data service to retrieve vehicle technical information.[49,50] The vehicle technical data included a diverse number of variables, most relevant of which were manufacturer make and model, fuel type, engine displacement, mass, type approval category, date of manufacture, and Euro status. The data are generally obtained from the Motor Vehicle Registration Information System (MVRIS).[51] Diesel Euro 6 vehicles were further manually classified by their known postcombustion NO_x control technology, either LNT or SCR systems. The classification of after-treatment technology used a number of sources, most notably Yang et al.,[52] and was conducted by an

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expert with extensive vehicle knowledge (Sujith Kollamthodi (Ricardo Energy & Environment), personal communication, August 2017). Seventy eight percent of diesel-powered Euro 6 passenger vehicles could be classified into these two additional groups.

Data. The data sets from the measurement campaigns were processed to conform to a formal relational data model outlined in the **emitr** R package, and the database system used was PostgreSQL.[53−55] The data set was filtered to contain a select set of vehicles with reliable and complete vehicle technical information. The data used in the analysis consisted only of vehicle type approval categories of M1 (passenger cars) and N1 (light-duty vans <3.5 tonnes), engine types of diesel and gasoline, and vehicles with Euro status between 3 and 6. This process resulted in a set with 300000 observations with approximately 201000 unique vehicle registrations. For counts of vehicles by their type, fuel type, and Euro status, see Table S2.

Meteorological observations were sourced from meteorological monitoring sites nearby the road sections used for remote sensing and were accessed from the NOAA Integrated Surface Database (ISD).[56] The meteorological observations were joined to the vehicle capture data so every capture had an ambient temperature, relative humidity, and wind speed and direction observation. However, the data sourced from the ISD are of hourly resolution but vehicles and their emissions can be captured every few seconds. To accommodate this, the hourly observations for each session were padded to generate a time series at second resolution. The missing observations between the hour observations were then interpolated with a linear function and joined to the captured set.

Data Analysis Approach. A single RSD measurement has a sampling time of 0.5 s and therefore each capture is a snapshot of a vehicle for a short duration which may or may not represent typical driving behavior. RSD measurements benefit from not being limited to single observations and typical behavior can be determined by using large numbers of observations. Many measurements, typically hundreds, are used to form useful conclusions and illuminate average patterns. Aggregations are often used with such data to obtain mean emissions and uncertainties for groups of observations.[7] However, here, a different approach is used with statistical modeling. Rather than performing aggregations using potentially arbitrary groups (for example, a narrow range in ambient temperature), generalized additive models (GAMs) with smooth functions were used to model the data.[57] GAMs allow a convenient way to explore nonlinear relationships among variables, and the application here is simple with only one dependent variable: ambient air temperature. Models such as these can also be used in a predictive way after being developed. The smoothers used for the GAMs were thin plate regression splines, and their basis dimension term (k) was set to four.[58] These calculations were conducted with the **mgcv** R package.[57]

Emission Prediction. The GAMs were used to predict NO_x emissions for different air temperatures and vehicle fuel types. If the air temperature was outside the observation space used for GAM calculation (between 0.5 and 25 °C), the prediction was forced to be the extreme edge of the calibration space to avoid using the models in conditions they had not been developed with (Figure S3). This approach resulted in the optimistic handling of predicted NO_x emissions below 0.5 °C and above 25 °C because it seems likely that NO_x emissions would continue to increase at lower temperatures than those experienced in the field campaigns.

To investigate the potential spatial patterns of NO_x emission based on air temperature, European modeled surface air temperature data (variable code `t2m`) between 2010 and 2017 were sourced from the European Centre for Medium-Range Weather Forecasts's (ECMWF) ERA Interim data product.[59] These data are gridded spatial raster objects and were used at the maximum spatial resolution available, 0.125 × 0.125 decimal degrees. The data were filtered to daytime periods (hours between 06:00 and 18:00) and then aggregated to annual and wintertime (December, January, February) means, and these summaries were then used to predict NO_x emissions. This spatial data manipulation was conducted with R and vector and raster extensions,[60−63] and the air temperatures used for prediction are shown in Figure S4. When calculating relative NO_x emissions, 20 °C was used as the relative temperature because this represents a conservative temperature for type approval conditions.

RESULTS AND DISCUSSION

Vehicular NO_x Emissions and Ambient Temperature. Light-duty diesel vehicle NO_x emissions were found to be highly dependent on ambient air temperature (Figure 2).

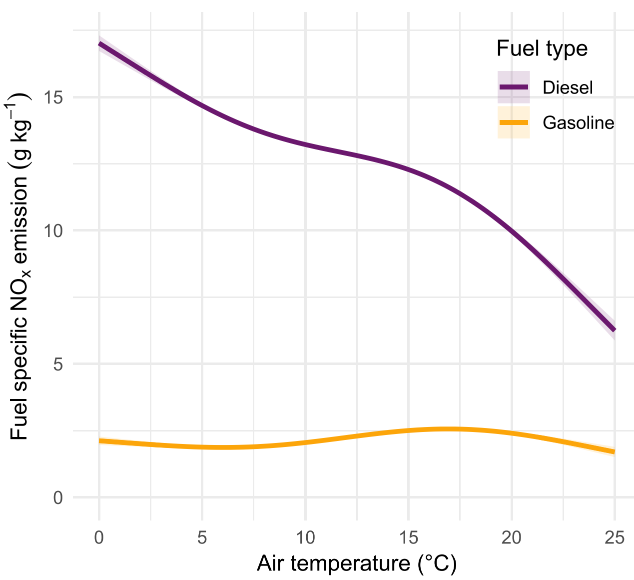

Figure 2. Generalized additive models (GAM) of NO_x emissions based on air temperature for light-duty diesel and gasoline-powered vehicles. The shaded zones represent the models' standard error for the prediction.

Diesel vehicles emitted the least NO_x at the highest ambient temperature encountered of 25 °C. Average diesel NO_x emissions decreased at a rate of -0.36 g kg^{-1} ° C^{1-} between 0 and 25 °C and had a range of 6.3 and 17g kg^{-1} (a difference of 10.8 g kg^{-1}). These results show that there is a significant "low temperature NO_x emission penalty" for diesel-powered light-duty vehicles. NO_x emissions from gasoline-powered vehicles showed very little evidence of dependence on ambient temperature (Figure 2). NO_x emissions from diesel vehicles were higher than gasoline vehicles and were over 10g kg^{-1} greater for temperatures below 14 °C (Figure 2). Diesel vehicle CO emissions showed no air temperature dependence, but gasoline-powered vehicles did display a slight low temperature

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penalty indicating that a small fraction of vehicles in the data set were captured below optimum operating temperature due to enriched fuel−air ratios (choking; not shown).

When diesel vehicles were split by their Euro standard, the older Euro 3 to 5 vehicles emitted NO_x in a similar way and could therefore be considered a distinct group (Figure 3). Euro 6 diesel vehicles emitted less NO_x and demonstrated a weaker absolute ambient temperature dependence compared to older vehicles compliant to preceding Euro standards. For manufacturers to achieve the diesel Euro 6 NO_x compliance, additional technological development was necessary in the form of new after-treatment technology. Two principal postcombustion after-treatment technologies have been widely adopted: LNT and SCR systems.[52] The use of these technologies represent a significant step in light-duty diesel vehicle emission control, and the remote sensing observations indicate that these devices make the fleet of Euro 6 diesel distinct from older vehicles compliant to preceding Euro standards (Figure 3).

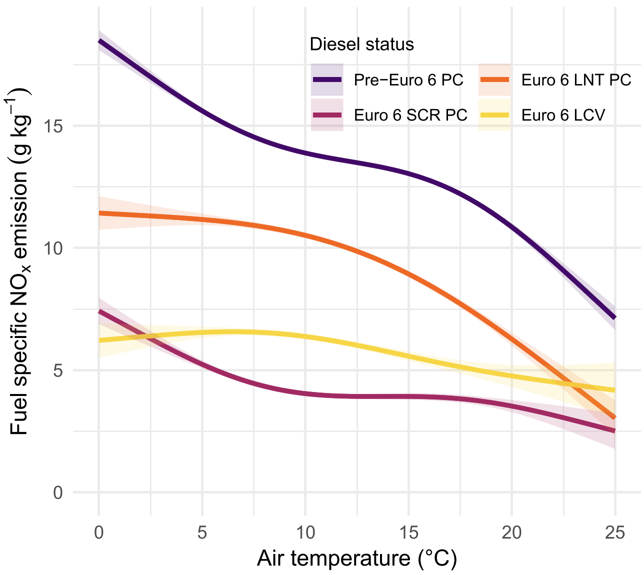

Figure 3. Generalized additive models (GAM) of NO_x emissions based on air temperature for groups of diesel-powered passenger vehicles. Passenger cars have been abbreviated to PC and further by their NO_x emission control technology: selective catalytic reduction (SCR) and lean NO_x traps (LNT). Euro 6 Light commercial vehicles (LCV) have also been displayed but without their emission control technology due to a small sample size. The shaded zones represent the models' standard error for the prediction.

The two types of postcombustion Euro 6 diesel NO_x control technology did however demonstrate markedly different ambient temperature responses (Figure 3). On average, vehicles with LNTs were less effective at reducing NO_x emissions when compared to those equipped with SCR. LNTs also demonstrated a stronger temperature dependence than SCR. Despite LNTs showing a greater NO_x penalty, LNT and SCR vehicles converge at higher temperatures and by 25 °C, NO_x emissions were similar, and this is within the temperature range where type approval test cycles are conducted. This convergence behavior could be interpreted as potential evidence for the so-called "thermal window" where NO_x emission controls, most notably exhaust gas recirculation (EGR), are optimized for temperatures where type approval testing procedures are conducted.[17,64,65] The better on-road NO_x control achieved by SCR over LNT has also been reported elsewhere with PEMS instrumentation.[23,24]

LNTs operate under a cycle of chemical adsorption and regeneration once NO_x saturation is reached. LNT store NO_x until their reduction rates drop below a threshold, and then a regeneration is initiated by a short period of fuel-rich combustion where exhaust temperatures increase. The NO_x stored in the trap is then reduced to nitrogen and emitted out the tailpipe. Certain operating conditions are necessary before regeneration can occur efficiently, and there is evidence that while LNT performance can be very good when used in open-road and constant speed conditions, their NO_x capturing performance can be very poor in urban driving conditions.[24] This is explained by inefficient regeneration or when regeneration is not triggered when NO_x saturation has occurred, most probably due to certain other operating conditions not being met. SCR technology does not rely on the same cyclical operation principle which could explain why SCR is shown to be a better NO_x control strategy on an average based on on-road remote sensing observations (Figure 3). These insights suggest that manufacturers will most likely need to embrace SCR technology (or a combination of SCR and LNT) rather than LNT alone to ensure compliance to the increasingly stringent future European NO_x emission limits which will be tested with real driving emission (RDE) tests.

Diesel LCV compliant to Euro 6 are also shown in (Figure 3). These vehicles showed little ambient temperature dependence, but uncertainty below 5 °C and above 20 °C was higher due to fewer vehicles being sampled. These vehicles are almost exclusively equipped with SCR, and therefore their NO_x emission behavior is more similar to SCR passenger vehicles than any other group.

Diesel emission factor multipliers based on type approval temperatures (assumed to be 20 °C) are shown in Table 2. These multipliers are analogous to conformity factors used for RDE tests and are of use for modellers and those preparing emission inventories. Interestingly, despite the lower absolute NO_x emissions by Euro 6 vehicles with identified after-treatment technologies (Figure 3), these vehicles still demonstrate a significant relative low temperature NO_x emission penalty (Table 2). However, because of much lower absolute emissions, the air quality consequences of this

Table 2. Relative NO_x Emission Factors from 20° C for Different Diesel Passenger Vehicles' Euro Statuses[a]

Vehicle type	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C
Pre-Euro 6 PC	1.67 ± 0.37	1.44 ± 0.12	1.28 ± 0.07	1.2 ± 0.09	1 ± 0.15	0.67 ± 0.47
Euro 6 PC	1.62 ± 0.45	1.51 ± 0.15	1.43 ± 0.09	1.32 ± 0.11	1 ± 0.19	0.52 ± 0.58
Euro 6 LNT PC	1.82 ± 0.63	1.78 ± 0.23	1.68 ± 0.12	1.42 ± 0.14	1 ± 0.26	0.51 ± 0.71
Euro 6 SCR PC	2.03 ± 0.49	1.48 ± 0.16	1.14 ± 0.1	1.11 ± 0.13	1 ± 0.25	0.72 ± 0.71

[a]The uncertainty around the emission factors represents the standard error of the GAM models' predictions.

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behavior will be far less severe when compared to pre-Euro 6 vehicles.

When pre-Euro 6 diesel vehicles were grouped by manufacturer, all manufacturers demonstrated evidence of a low temperature NO_x emission penalty (Figure 4). The two highest-emitting manufacturer groups, General Motors (GM) and Mazda had penalties of 9 and 8.6 g kg^{-1} while BMW and Mitsubishi, the least polluting groups, had penalties of 2.4 and 2.6 g kg^{-1}. These findings demonstrate that some manufacturers on average had superior NO_x control than others for their pre-Euro 6 diesel vehicles. Figure 4 also shows evidence of two groups of emission behavior, perhaps demonstrating manufacturers' preference for certain technology or strategies for NO_x emission control. The differential in emissions performance and temperature dependence seen between the different manufacturers could have implications for NO_x emissions throughout Europe. For example, countries with higher proportions of pre-Euro 6 diesel GM and Mazda vehicles in the fleet would tend to be associated with higher overall emissions of light-duty diesel NO_x emissions.

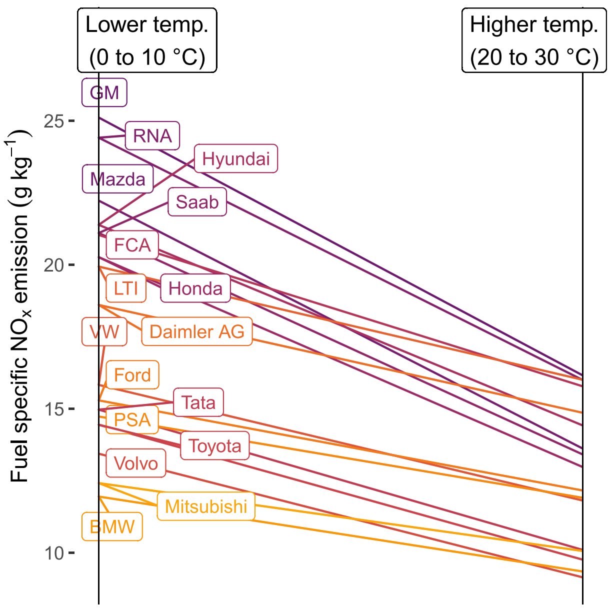

Figure 4. Average NO_x emissions for pre-Euro 6 diesel light-duty vehicles by manufacturer group between 0−10 and 20−30 °C. Only groups with at least 40 captures have been displayed, and full manufacturer group names can be found in Table S3.

Despite the focus on ambient temperature, changes in absolute humidity could be a contributory factor to help explain the results presented. Absolute humidity in cooler periods tends to be lower than during warmer periods (Figure S5), and because NO_x emissions are inversely related to humidity, some of the identified low temperature penalty could be driven by low humidity conditions.[29] However, when NO_x emissions were adjusted for ambient humidity by a common technique in an attempt to explain the dependence on ambient temperature (Equation S1),[33] the results showed a small reduction in NO_x emissions relative to ambient humidity (Figure S6) but could not explain the observed behavior seen in Figure 2 or Figure 3. Therefore, reduction in absolute humidity was a small contributing factor which did not explain the observations presented. It should also be recognized that it is questionable whether existing adjustment factors are suitable for modern light-duty vehicle fleets when characterizing their on-road and in-service emissions.

Air Quality Implications. Roadside NO_x concentrations tend to be at their highest during periods of low temperatures, and this is generally attributed to meteorological conditions being less favorable for pollutant dispersion and transportation, specifically high atmospheric stability and a lack of wind (for example, Figure S7).[66] The low temperature NO_x emission penalty demonstrated for diesel vehicles by remote sensing would have exacerbated the effect of stagnant atmospheric conditions and added an additional NO_x burden to the

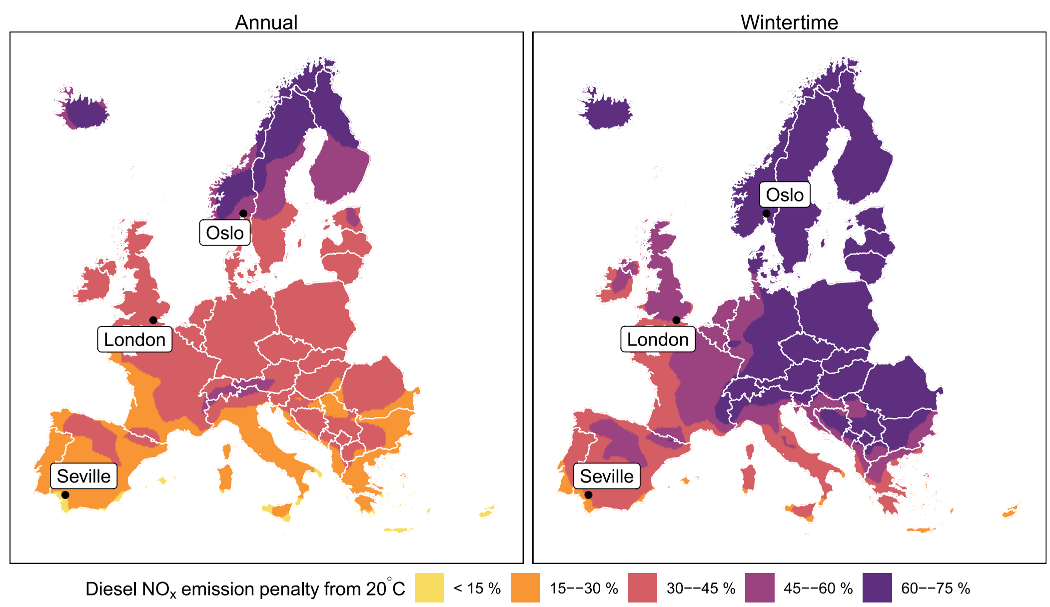

Figure 5. Light-duty diesel NO_x emission penalties when considering average daytime annual and wintertime air temperatures throughout Europe and fleet mix captured by the on-road remote sensing field campaigns. The diesel low NO_x emission penalty has been defined as the difference between NO_x emission for the locations' mean air temperature and the NO_x emission at 20 °C. The labeled cities are discussed in text.

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roadside atmosphere, which has not been accounted in emission inventories. This additional NO_x loading to the roadside atmosphere would be especially important to consider during poor air quality episodes when temperatures remain low for several days and fresh emissions sequentially add to previously emitted pollutants.

The increased NO_x emissions at low temperature from light-duty diesel vehicles would be influential for poor air quality episodes in most European locations since the mid-1990s when diesel vehicles began to significantly penetrate the passenger vehicle fleet.[67] This effect would be especially important for cooler European countries or cities such as those located in the high latitudes, located inland, or at altitude.

Figure 5 demonstrates the spatial heterogeneity of the diesel low temperature NO_x emission penalty throughout Europe using all light-duty vehicles during the 2017 and 2018 on-road remote sensing field campaigns. Urban areas located in Europe's warmest areas such as Seville, southern Spain have suffered the smallest diesel NO_x penalty, while cities located inland and in the higher latitudes were affected to a much greater extent. Oslo (Norway) along with most of the Scandinavian Peninsula and the Baltic States (Estonia, Latvia, and Lithuania) have been burdened with up to 75% greater NO_x emissions during the winter compared to NO_x emissions at a temperature where type approval testing is performed. Even cities such as London which experience mild and maritime climates have still been burdened with 30−45% and 45−60% greater NO_x emissions from their passenger diesel vehicle fleet during the entire year and wintertime, respectively (Figure 5). Considering Europe as a whole, the low temperature emission penalty represents an average of 38% greater NO_x emissions when compared to emissions at 20 °C when using annual mean temperatures.

Using annual mean temperature as a metric, the coldest urban areas in Europe are located in the Baltic and Nordic regions. The urban areas located in these locations can expect to observe a decrease in their roadside NO_x concentrations at a faster rate compared to areas which experience warmer climates if the rates of passenger vehicle turnover are similar among the different locations. As the older, pre-Euro 6 diesel vehicles (with a strong absolute temperature dependence for NO_x emissions) are removed from service and replaced with new diesel vehicles compliant to the current Euro 6 standards and better after-treatment technologies or with gasoline, hybrid, or electric vehicles, the importance of the low temperature NO_x emission penalty for air quality will diminish. This decrease can be expected without any further management or intervention efforts. This effect only relies on the continuity of natural passenger fleet turnover and the current European market-shift away from diesel-powered vehicles, which indicates a positive outlook for European roadside air quality and the compliance to NO_2 ambient air quality limits.

Using Oslo and London as case studies, wintertime NO_x emissions in these cities can be compared to those predicted at a fixed 20 °C (Figure 6). At 20 °C, the reduction in NO_x emissions when comparing a pre-Euro 6 diesel and Euro 6 vehicles equipped with SCR is 7.3 g kg^{-1}. However, for London and Oslo, this difference increases to 10.2 and 11 g kg^{-1}, respectively, during the winter (Figure 6). Therefore, taking account of the ambient temperature dependence, there is a greater absolute reduction in NO_x emissions when compared to not considering temperature, which reinforces the positive outlook for European roadside NO_x concentrations. In the case of London and Oslo, this reduction is 40 and 51% greater than predicted in the case where no temperature dependence is considered, respectively. Vehicle fleets composed entirely of gasoline-powered vehicles are also shown for contrast in Figure 6 and demonstrate the difference of NO_x emissions between the two fuel types.

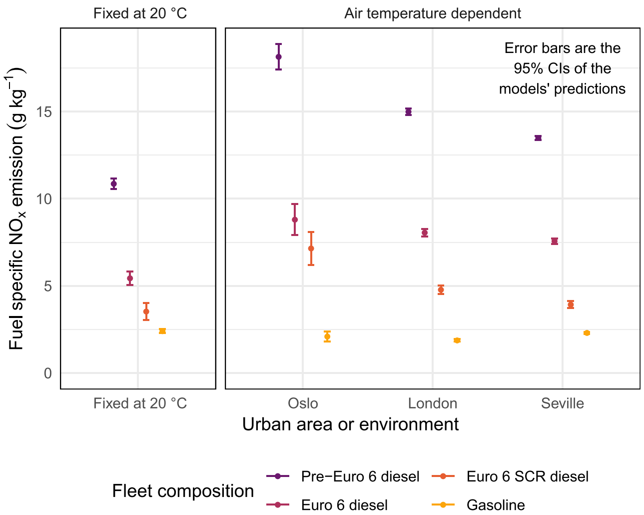

Figure 6. Predicted NO_x emissions for four passenger fleet composition scenarios during the wintertime for three European urban areas which experience different climates and at a fixed 20 °C.

In the wake of the Volkswagen diesel emission scandal, diesel vehicles have become less attractive than they once were in Europe.[68] New diesel car sales show a sharp decrease between 2011 and 2017 where new diesel sales went from 56% to 44% of total vehicles and is expected to continue to decrease (Figure S8).[67] The demand for and sales of passenger vehicles has not declined during the same period, so this shortfall is being met by increases in sales of gasoline-powered vehicles but also a growing portion of hybrid or electric vehicles.[67,68] In many European countries, the incentivisation of diesel vehicles, which was introduced in the mid-2000s, has been removed and extra taxes have been applied to diesel fuel and diesel vehicles. At the same time, hybrid or electric vehicles have experienced a range of governmental subsidies increasing their attraction to consumers and boosting their new car sales.[69] All these factors contribute to a positive outlook for NO_x emissions because the vehicles that demonstrate the most severe NO_x penalty are being removed from service as the passenger vehicle market changes. There is also evidence that the amount of NO_2 produced by light-duty diesel vehicles decreases with increasing vehicle mileage.[70] This observation offers yet another aspect which reinforces an optimistic outlook for European roadside NO_x and NO_2 concentration reduction.

This work exclusively frames vehicular NO_x emissions in a roadside air quality context. However, NO_x is a very important species to consider for ozone (O_3) and particulate matter (PM) formation, which are of importance from a human health perspective. The influence of the diesel low temperature NO_x emission penalty requires consideration by the O_3 and PM modeling communities because it represents precursor emission rates which are dependent on ambient temperature; this is not currently implemented and would likely alter predicted concentrations of these (and other species), especially when considering seasonal effects. For example, it may be that existing modeling underestimates wintertime NO_x

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emissions but overestimates summertime NO_x emissions, which would have implications for the generation of secondary pollutants. Similarly, this work only explores the European environment, but it is relevant to other markets such as the United States, even with their far lower penetration of diesel passenger vehicles because the low temperature NO_x penalty will still be active in other markets.

This work discusses on-road emission measurements within an ambient temperature range of 0.5−25 °C. Follow-up work should aim to extend this temperature range. To extend these temperatures, cooler and warmer locations outside the United Kingdom need to be targeted with the same on-road remote sensing technique so the lower and higher temperatures relevant to the European and other climates can be added to a future analysis and characterized.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01024.

> Details of the gas cylinders used for the field calibrations, counts of captured vehicles based on vehicle type, full names of manufacturer groups, number of vehicle captures, mean NO and NO_2 emissions as captured for both RSD instruments, an example of GAM extrapolation behavior, mean annual and wintertime surface air temperatures for Europe, mean monthly absolute humidity for selected European cities, generalized additive models (GAM) of NO_x emissions with and without humidity corrections applied, ambient NO_x concentrations dependence on air temperature, market share of diesel-powered passenger vehicles, and equation used to correct NO_x emissions for ambient humidity (PDF)

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Notes

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