



# Article Impact of Illegal Application of Urea Regulator on Real-World Exhaust Nitrogen Oxygen and Particle Number Emissions

Jingyuan Li<sup>1,2,3</sup>, Maodong Fang<sup>2</sup>, Zhiwen Yang<sup>2,3</sup>, Zongyan Lv<sup>4</sup>, Ning Wei<sup>4</sup>, Fuwu Yan<sup>1,\*</sup> and Hongjun Mao<sup>4</sup>

- <sup>1</sup> Hubei Key Laboratory of Advanced Technology for Automotive Components, School of Automotive Engineering, Wuhan University of Technology, Wuhan 430070, China
- <sup>2</sup> National Engineering Laboratory for Mobile Source Emission Control Technology, China Automotive Technology and Research Center Co., Ltd., Tianjin 300300, China
- <sup>3</sup> Light Vehicle Emission and Energy-Saving Testing and Research Department, CATARC Automotive Test Center (Tianjin) Co., Ltd., Tianjin 300300, China
- <sup>4</sup> Tianjin Key Laboratory of Urban Transport Emission Research, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China
- \* Correspondence: yanfw@whut.edu.cn

Abstract: Urea regulators (UR) have generally been employed against diesel trucks to save urea usage and thus contribute to the reduction in excessive emissions, while their usage is generally difficult to supervise and enforce. By conducting real driving emission measurements on a China IV heavy-duty diesel truck, a "trade-off" effect caused by UR was found between nitrogen oxides (NOx) and particle number (PN) emissions. The usage of UR contributes to 1.04 times higher NOx but 0.28 times lower PN emissions for the whole trip. In particular, the increasing effects on NOx are most efficient on the highway and least effectual on the urban road, while the decreasing effects on PN exhibit an opposite trend under different road types. From low- and medium- to the high-speed bin, the peak average vehicle-specific power NOx emission rates exhibit markedly increasing but slightly decreasing trends for the truck with and without UR, respectively. Furthermore, the NOx emissions in units of CO<sub>2</sub> and the linear correlational relationship between CO<sub>2</sub> and NOx instantaneous mass emission rates, especially those on the highway, are significantly enhanced. This study directly clarifies the effects of UR on real-world emissions, providing a scientific basis for the real-time identification of the malfunction of the selective catalytic reduction system.

Keywords: urea regulator; diesel truck; NOx; PN

# 1. Introduction

Motor vehicles have gradually emerged as an increasingly prominent anthropogenic source of particulate matter (PM) and nitrogen oxides (NOx), thus leading to a negative effect on air quality and human health [1–4]. According to the latest source analysis against  $PM_{2.5}$  [5], mobile exhaust emissions mainly contributed by vehicles have become the primary or secondary regional source for some megacities in China. In particular, heavy-duty diesel trucks (HDDTs), accounting for about 7.0% of the total vehicle fleet, have been investigated to contribute to 70.1% of NOx and 51.5% of PM emissions from all vehicles across China in 2021 [6]. Moreover, as a vital precursor for ozone (O<sub>3</sub>) and PM, NOx emitted by diesel trucks will pose certain challenges to the collaborative governance of PM and O<sub>3</sub> [7] during China's 14th Five-Year Plan period. Consequently, emission control against HDDTs will still be essential to improve urban air quality in the future.

To alleviate the exhaust emissions of HDDTs, various efforts have been employed around the world, including the implementation of stringent standards for new vehicles [8], the retirement of old high-emission vehicles [6,9], and inspection and maintenance measures for in-use vehicles [10]. Considering the huge proportion of in-use vehicles and the relative lack of effective regulatory approaches, emission control against in-use diesel trucks will



Citation: Li, J.; Fang, M.; Yang, Z.; Lv, Z.; Wei, N.; Yan, F.; Mao, H. Impact of Illegal Application of Urea Regulator on Real-World Exhaust Nitrogen Oxygen and Particle Number Emissions. *Atmosphere* **2022**, *13*, 1739. https://doi.org/10.3390/ atmos13101739

Academic Editor: Giorgio Martini

Received: 19 September 2022 Accepted: 17 October 2022 Published: 21 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). be essential to mitigate vehicle exhaust pollution. Nowadays, remote on-board diagnostic (OBD) is increasingly becoming an important way in China to monitor the real-time operating and emission conditions of in-use heavy-duty vehicles [11,12]. The data collected from OBD are also proven to be consistent with that obtained from portable emission measurement systems (PEMS) [13]. For now, the remote OBD system is mostly used to count fuel consumption, NOx emission, OBD fault information, etc. However, the effect of the remote OBD method is not fully realized due to its lack of supervision methods, such as the identification of causes of excessive emission.

As an important part of emission control against diesel trucks, the selective catalytic reduction (SCR) system was proven to effectively reduce NOx emissions [14,15] but also enhance the formation of ammonia-induced particles [16–20]. The NOx reduction effectiveness of the SCR can be influenced by factors such as the driving condition [15], fuel quality, urea injection [21], etc. Meanwhile, the urea injection can be reduced or avoided by taking cheating approaches including the illegal application of urea emulator [22], urea shielding, and urea regulator (UR). Due to its convenient installation and low cost, the UR that can reduce the amount of urea injection are widely applied to diesel trucks for urea-saving, but rarely receive effective supervision. In addition, most studies are focused on the mechanism of the SCR on the emission influence of the UR on NOx and particle number (PN) emissions emitted by diesel trucks under real-world driving conditions. Therefore, real-world emission measurements will be of immense necessity to clarify the changes in the NOx and PN emission characteristics and to obtain a scientific method for the real-time identification of the malfunction of the SCR caused by the usage of the UR.

This study aims at acquiring a scientific method for the real-time identification of SCR malfunction by investigating the characteristics of NOx and PN emissions emitted by diesel trucks both with and without the usage of UR. Real driving emission measurements with a PEMS against a China IV HDDT were conducted on a complicated route, consisting of urban roads, rural roads, and highways. The effectiveness of the UR on both NOx and PN emissions is directly investigated by driving the diesel truck on the test route with and without the UR. To fully obtain the effects of the UR on different components of the pollutants, the NOx was divided into nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), while the particles with an aerodynamic particle size ranging from 6 nm to 2.5  $\mu$ m were divided into solid >23 nm and total <23 nm particles. Specifically, the effectiveness of the UR on those pollutants was investigated by successively comparing the differences in instantaneous volumetric concentration distribution, emission factors (EFs), and vehicle-specific power (VSP)-bin emission rates between the situation with and without UR. Moreover, the effects of the UR on the variations in the correlation between NOx and carbon dioxide (CO<sub>2</sub>) instantaneous mass emission rates under different road types are also clarified.

#### 2. Materials and Methods

### 2.1. Test Vehicle and Route

Table 1 demonstrated the specifications of the tested China IV HDDT, which is equipped with SCR but without DOC and DPF [23]. Due to the large share in the diesel truck fleet, the poor emission control levels, and the susceptibility to illegal operations for China IV HDDTs, a China IV HDDT is thus selected to investigate the effect of the UR on emissions. The particle emission control of the tested truck was mainly achieved by reducing the generation of particulate matter during the combustion process of the engine through fuel injection and combustion optimization technology, while the NOx emission control relied on the SCR to reduce NOx emissions during the off-engine post-processing. Normally, an alarm system will be automatically activated when the truck lacks urea or the urea injection system is manually turned off, which can be supervised by the OBD. However, the alarm system can be bypassed through the illegal application of the urea regulating screw, called UR here. By installing a UR on the exhaust temperature sensor, the perceived temperature can be regulated by adjusting the depth of the exhaust temperature

sensor, thereby reducing the urea injection. In addition, the fuel and urea employed here were obtained directly from the local market.

Table 1. Test vehicle specifications.

Parameters	Truck	
Vehicle brand	Jiefang	
Vehicle type	Box stake	
Fuel type	Diesel	
Gross/Curb weight (t)	31.0/12.7	
Displacement (L)	7.7	
After-treatment	SCR	
Emission standard	China IV	
Model year	2016	
Odometer (km)	185,205	
Gear	manual 8	

To fully investigate the influence of the UR on real driving NOx and PN emissions, a complicated test trip (~51 km) consisting of urban roads, rural roads, and highways was selected to perform real-world emission measurements in July 2018. The tested route mostly consisted of rural roads and highways compared to urban roads due to the main activity area of the tested truck being located in the non-urban area. To avoid the emission differences caused by the inconsistent driving behaviors between different drivers, one local driver was arranged to alternate driving the truck with and without UR on the trip during the test. The number of the tested trips both with and without UR was 3 on the selected route. To reflect the emission differences under different driving conditions, the road types herein were simply categorized as the urban road (V  $\leq$  30 km/h), rural road (30 < V  $\leq$  60 km/h), and highway (V > 60 km/h) based on the instantaneous vehicle speed and actual speed distribution in different activity areas. The summary of driving characteristics for the real driving tested truck with and without UR under different road types was demonstrated in Table 2. It was clear that no obvious differences in driving parameters can be found with and without UR, even regardless of road type.

Parameters	Urea State	Urban	Rural	Highway	Whole Trip
Trip distance (km)	with UR without UR	$5.5 \pm 0.2$ $5.2 \pm 0.1$	$25.9 \pm 1.0$ $26.1 \pm 0.7$	$19.5 \pm 0.2$ $19.7 \pm 0.7$	$50.9 \pm 0.6$ $51.2 \pm 0.3$
Avg. speed (km/h)	with UR without UR	$10.7 \pm 0$ $10.4 \pm 0.7$		$77.2 \pm 5.0$ $80.4 \pm 1.3$	$37.8 \pm 1.3$ $38.2 \pm 0.8$
Avg. RPA (m/s <sup>2</sup> )	with UR without UR	$\begin{array}{c} 0.17\pm0.04\\ 0.19\pm0.02\end{array}$	$\begin{array}{c} 0.09 \pm 0.01 \\ 0.09 \pm 0.01 \end{array}$	$\begin{array}{c} 0.04\pm 0\\ 0.05\pm 0\end{array}$	$\begin{array}{c} 0.08 \pm 0.01 \\ 0.08 \pm 0.01 \end{array}$
Idle (%)	with UR without UR	$\begin{array}{c} 30.0\pm1.5\\ 27.9\pm1.0\end{array}$	0 0	0 0	$\begin{array}{c} 11.6 \pm 0.9 \\ 10.6 \pm 1.2 \end{array}$
Acceleration (%)	with UR without UR	$\begin{array}{c} 29.7\pm4.6\\ 31.7\pm1.2 \end{array}$	$\begin{array}{c} 28.8 \pm 3.0 \\ 28.1 \pm 4.7 \end{array}$	$\begin{array}{c} 11.2\pm1.6\\ 11.6\pm0.2 \end{array}$	$25.9 \pm 3.5$ $26.3 \pm 2.1$
Cruise (%)	with UR without UR	$\begin{array}{c} 17.8\pm5.9\\ 14.5\pm2.3 \end{array}$	$\begin{array}{c} 48.4\pm4.5\\ 49.3\pm8.8\end{array}$	$\begin{array}{c} 77.8\pm1.1\\ 77.5\pm0.6\end{array}$	$\begin{array}{c} 42.1\pm4.3\\ 41.5\pm4.9\end{array}$
Deceleration (%)	with UR without UR	$\begin{array}{c} 22.6\pm2.7\\ 26.0\pm0.1 \end{array}$	$\begin{array}{c} 22.9 \pm 1.5 \\ 22.7 \pm 4.2 \end{array}$	$\begin{array}{c} 11.0 \pm 0.4 \\ 11.0 \pm 0.5 \end{array}$	$\begin{array}{c} 20.6 \pm 1.8 \\ 21.7 \pm 1.6 \end{array}$

Table 2. Driving characteristics.

### 2.2. Measurement System

The real-time instantaneous and cumulative exhaust emissions of gaseous pollutants and particles were collected by a united PEMS consisting of a SEMTECH-DS Gas unit and a renewed electrical low-pressure impactor (ELPI+). The SEMTECH-DS [24], developed by Sensors Inc., adopts a non-dispersive ultraviolet (NDUV) sensor to acquire concentrations of NO and NO<sub>2</sub>, a non-dispersive infrared (NDIR) sensor to measure CO and  $CO_2$ , and other detectors for other gaseous pollutants. Moreover, several other units fixed around the vehicle body were also included, such as a SEMTECH High-Speed Exhaust Flow Meter (SEMTECH EFM-HS) to continuously and directly monitor the vehicle exhaust flow, a temperature probe to monitor the exhaust temperature near the exit of the tailpipe, a GPS to acquire vehicle speed and location information (i.e., altitude, latitude, and longitude), and a weather probe for the ambient temperature and relative humidity. To prevent the generation of condensates and high molecular weight hydrocarbons during the test periods, the sampling tube between the EFM and SEMTECH-DS analyzer was heated and maintained at 190 °C. Meanwhile, the ELPI+ [25] (Dekati Ltd. Kangasala, Finland) with 14 stages was utilized to measure aerodynamic particle size distribution and number concentrations over a diameter range of 6 nm-10 µm. Additionally, a Dekati Engine Exhaust Diluter (DEED) [26], installed before the ELPI+, was used to remove semi-volatile particles. Two stages of dilution were selected and an overall dilution ratio of 100 was set during this test. Specifically, the sample flow was firstly heated to 150 °C and diluted 10 times at the first dilution stage, then heated to 300~400 °C to remove volatile organic compounds through the evaporation tube, and ultimately diluted 10 times and cooled to ambient temperature at the second dilution stage. On the basis of the nominal particle size measured by each stage, the first 6 stages with diameters below 23 nm and the stages 7–12 with a measuring range from 23 nm to 2.5  $\mu$ m, were used to estimate, respectively, in total <23 nm and solid (23 nm~2.5  $\mu$ m) particle emissions.

To ensure that the vehicle engine operation will not be affected by the power demand of the device, an extra gasoline generator was employed to power the PEMS instrument. All data acquired in this study were recorded at a frequency of 1 Hertz. The whole PEMS together with the co-driver and other cargo loads, with a total weight being around 2900 kg, resulted in around 22.8% of the curb weight of the tested truck. To ensure the accuracy of the PEMS, routine calibrations before and after tests of gaseous and particle pollutants were conducted by controlling for the zero and span drift of the gaseous analyzers, purging and verifying the zero flow of the EFM, and executing flush and zero calibrations for the electrometer in the ELPI+. Moreover, due to the different response times for instruments, time synchronization of data acquired by different devices was performed before data analysis. Moreover, a laptop computer, connected to the instrument by the local area network, was employed to monitor the real-time operational status of the device.

#### 2.3. Vehicle-Specific Power (VSP)

To further reflect the effectiveness of the usage of UR on emissions under various driving conditions, VSP, namely the instantaneous engine power demand per vehicle unit mass (kW/ton), was used to illustrate the correlation between vehicle operating modes and exhaust emissions. According to the motor vehicle emission simulator (MOVES) [27], VSP can be calculated as the following Equation (1):

$$VSP = \frac{Av + Bv^{2} + Cv^{3} + Mv(a + gsin\theta)}{f_{scale}}$$
(1)

where M is the gross vehicle weight (tons), v is the vehicle speed (m/s), a is the vehicle acceleration (m/s<sup>2</sup>), g is the gravitational acceleration (9.81 m/s<sup>2</sup>),  $\theta$  is the road grade (radians), and f<sub>scale</sub> is the fixed mass factor (tons). Additionally, A (kW s/m), B (kW s<sup>2</sup>/m<sup>2</sup>), and C (kW s<sup>3</sup>/m<sup>3</sup>) represent the coefficients of the rolling resistance, rotational resistance, and aerodynamic drag, respectively. Obtained from the MOVES model [27], the values of A, B, C, and f<sub>scale</sub> coefficients are 2.0491, 0, 0.004195, and 17.1, respectively, for the tested truck.

# 3. Results and Discussion

# 3.1. Effects on Nitrogen Oxides Emissions

3.1.1. Effects on NOx Instantaneous Volumetric Concentrations

Obvious differences occurred in the density distributions of NO and NO<sub>2</sub> instantaneous volumetric concentrations for the situation with and without UR (Figure 1). The height of the histogram herein represents the density, while the kernel density estimation curve represents a smoothed histogram that can demonstrate the distribution characteristics of data. Since the differences in driving conditions with and without UR are negligible (Table 2), it can be assumed that the change in concentration distribution is caused by the use of UR. For NO concentrations, an obvious bimodal distribution (mode concentration: 50 and 400 ppm) occurred for the vehicle without UR, while a trimodal distribution (mode concentration: 500, 950, and 1200 ppm), mostly attributed to the various driving conditions during the tested trip with different road types, was observed for the vehicle with UR. Consistent with the larger mode concentrations caused by the usage of the UR, the distribution of the NO concentrations around 500 ppm and above 800 ppm also exhibited larger densities. For NO<sub>2</sub> concentrations, a unimodal distribution occurred for the vehicle both without and with UR, but the mode concentration of the vehicle with UR (7 ppm) was relatively larger than that without UR (4 ppm). Additionally, larger distribution densities of NO<sub>2</sub> concentrations above 7 ppm were observed due to the usage of UR. Associated with increased mode concentrations and distribution densities at high concentrations, the min, max, 25th, 50th, and 75th percentile of the NO and NO<sub>2</sub> concentrations were also found to be markedly increased by the illegal application of the UR (Figure 1). These phenomena are probably related to the fact that the NO and NO<sub>2</sub> with large concentrations mostly emitted under severe driving conditions cannot be effectively reduced by the malfunction of the SCR caused by the UR.



**Figure 1.** Comparison of the density distributions for NO (**a**) and NO<sub>2</sub> (**b**) volumetric concentrations with and without the illegal application of urea regulator.

# 3.1.2. Effects on Distance-Based NOx Emission Factors

The trip-average NO, NO<sub>2</sub> and NOx EFs under different road types for the tested truck with and without UR are displayed in Table 3. The increase ratio (IR: %) in Table 3 was utilized to describe the increased effect of the application of the UR on NOx emissions. From the real-world emission results, we observe that the usage of the UR can contribute to enormously increased effects on NO, NO<sub>2</sub>, and NOx emissions but negligible decreased effects on CO<sub>2</sub> emissions. This fact may further prove that the differences in pollutant emissions between the situations with and without UR are mainly caused by the application of the UR rather than the subtle differences in driving behaviors between the trip tests with and without UR (Table 2). The application of the UR can result in 3.8 and 2.1, 0.7 and 0.9, and 0.3 and 0.7 times higher NO and NO<sub>2</sub> EFs under highways, rural roads, and urban roads, respectively. The increased effect of the UR on NO and NO<sub>2</sub> both exhibited a decreasing trend from the highway and rural roads to urban roads. This fact was mainly due to the increasing benefit of increased exhaust gas temperature on urban roads, rural

roads to highways for improving the NOx conversion efficiency of SCR with appropriate urea [15,28].

Road Type	Urea State	CO <sub>2</sub> (g/km)	NO (g/km)	NO <sub>2</sub> (mg/km)	NO <sub>x</sub> (g/km)
Highway	with UR without UR IR (%)	$726.4 \pm 52.5 \\ 726.6 \pm 6.6 \\ 0$	$\begin{array}{c} 10.6 \pm 1.3 \\ 2.2 \pm 0.1 \\ 385.0 \end{array}$	$\begin{array}{c} 102.7 \pm 9.0 \\ 32.9 \pm 8.9 \\ 212.2 \end{array}$	$\begin{array}{c} 10.7 \pm 1.3 \\ 2.2 \pm 0.1 \\ 382.4 \end{array}$
Rural	with UR without UR IR (%)	$\begin{array}{c} 770.9 \pm 14.9 \\ 771.5 \pm 23.6 \\ -0.1 \end{array}$	$\begin{array}{c} 10.9 \pm 0.1 \\ 6.5 \pm 0.2 \\ 69.2 \end{array}$	$\begin{array}{c} 106.9 \pm 2.9 \\ 54.9 \pm 6.9 \\ 94.5 \end{array}$	$\begin{array}{c} 11 \pm 0.1 \\ 6.5 \pm 0.2 \\ 69.5 \end{array}$
Urban	with UR without UR IR (%)	$\begin{array}{c} 1430.3 \pm 62.9 \\ 1506.9 \pm 86.5 \\ -5.1 \end{array}$	$\begin{array}{c} 21.6 \pm 0.4 \\ 16.9 \pm 0.7 \\ 27.9 \end{array}$	$\begin{array}{c} 277.7 \pm 10 \\ 160.3 \pm 20.8 \\ 73.2 \end{array}$	$\begin{array}{c} 21.9 \pm 0.4 \\ 17.1 \pm 0.6 \\ 28.3 \end{array}$
Whole trip	with UR without UR IR (%)	$\begin{array}{c} 825.4 \pm 30.3 \\ 828.0 \pm 17.1 \\ -0.3 \end{array}$	$\begin{array}{c} 12.0 \pm 0.6 \\ 5.9 \pm 0.1 \\ 104.0 \end{array}$	$\begin{array}{c} 123.7 \pm 4 \\ 56.8 \pm 10.3 \\ 117.7 \end{array}$	$\begin{array}{c} 12.1 \pm 0.6 \\ 5.9 \pm 0.1 \\ 104.1 \end{array}$

Table 3. On-road nitrogen oxides EFs of the tested truck on different road types.

Despite the slightly higher increased effects of the UR on  $NO_2$  (117.7%) compared to that on NO (104.0%) for the whole trip, distinct different increased effects between NO and NO<sub>2</sub> emissions occurred for different road types. The increased effect on NO was higher than that on  $NO_2$  for highways, while lower for rural roads and especially for urban roads. This is probably because the active operation window with a working temperature between 300 and 400 °C for the main NOx-SCR reaction of  $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (the "standard SCR" reaction) against NO conversion [19] is more achievable in highway driving conditions, thus leading to obvious higher increased effects on NO compared to NO<sub>2</sub> on the highway. For rural and urban roads, however, the "fast SCR" reaction of  $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$  mainly controlled by the availability of  $NO_2$  will be considerably faster than the "standard SCR" reaction due to the decreasing working temperature from highway, rural road to urban road [19]. Meanwhile, excess  $NO_2$  will also react with NH<sub>3</sub> via the "NO<sub>2</sub>-SCR" reaction of  $4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$  for those on rural and urban roads [19]. These phenomena thus resulted in distinguished higher increased effects of the UR on  $NO_2$  compared to that on NO on the rural road, especially on the urban road with extremely low exhaust temperature.

# 3.1.3. Effects on VSP-Bin NOx Emission Rates

Figure 2 shows the average mass emission rates of NO and NO<sub>2</sub> of the truck with and without UR in various VSP and speed bins. Compared to the variations in the average VSP-bin NO and NO<sub>2</sub> emission rates of the vehicle without UR, those average emission rates with UR also exhibited more distinguished increasing trends in all speed ranges, especially in the high-speed ranges. Moreover, the average emission rates of NO and NO<sub>2</sub> in different bins, especially those in the high-speed ranges, are generally higher for the truck with UR compared to that without UR. Specifically, the application of the UR resulted in 0.2 and 0.7, 1.6 and 1.5, and 5.1 and 2.1 times higher average NO and NO<sub>2</sub> emission rates under low-, medium-, and high-speed range for NO compared to NO<sub>2</sub>, while in the low-speed range for NO<sub>2</sub> compared to NO.



**Figure 2.** Comparison of average VSP-bin NO ( $\mathbf{a}$ ) and NO<sub>2</sub> ( $\mathbf{b}$ ) mass emission rates between the situation with and without the illegal application of urea regulator.

The highest emission rates of NO and NO<sub>2</sub> are both located in the high-VSP and high-speed bin for the truck with UR, which is mainly related to the fact that the increased combustion temperature caused by severe engine load can contribute more to the production of NOx [29]. However, the highest emission rates of NO and NO<sub>2</sub> are both located in the high-VSP and low-speed bin for the truck without UR, which is likely due to the reduced effect of the SCR on NOx emissions, especially those in high-speed driving conditions with high exhaust temperature. Meanwhile, the peak VSP-bin NOx emission rates exhibited markedly increasing but slightly decreasing trends from low and medium to the high-speed bin for those with UR and without UR, respectively.

## 3.2. Effects on Particle Number Emissions

# 3.2.1. Effects on PN Instantaneous Volumetric Concentrations

As demonstrated in Figure 3, the density of solid >23 nm and total <23 nm PN instantaneous volumetric concentrations for the vehicle with and without UR both exhibited a unimodal distribution. Contrary to the negative effect on the control of NO and NO<sub>2</sub> emissions due to the usage of the UR, a positive control effect occurred for PN emissions. This is mainly attributed to the fact that the limited urea injection caused by the employment of the UR can reduce exhaust ammonia which can form particles [30]. This evidence also indicates that a large number of HDDTs on the road today may produce extra particles related to the urea-SCR operation [19].



**Figure 3.** Comparison of the density distributions for total <23 nm (**a**) and solid >23 nm (**b**) PN volumetric concentrations with and without the illegal application of urea regulator.

8 of 12

Compared to the slight differences in the density distribution between with and without UR for solid >23 nm PN concentrations, an obvious smaller mode concentration and lower density of the particle with concentrations above  $2.0 \times 10^6$  #/cm<sup>3</sup> occurred for the total <23 nm PN concentrations when the UR was applied. Meanwhile, the minimum, maximum, 25th, 50th, and 75th percentiles of the total <23 nm PN concentrations were also found to be markedly reduced, due to the illegal application of UR as shown in Figure 3. The usage of the UR can more effectively weaken the production of the total <23 nm particles compared to solid >23 nm particles, mainly explained due to the nanoparticles being more easily produced during the SCR normal working conditions with proper urea injection [31].

# 3.2.2. Effects on Distance-Based PN Emission Factors

Table 4 presents the trip-average EFs of total <23 nm and solid >23 nm PN under different road types for the tested truck with and without UR. The total <23 nm PN EFs for the vehicle with and without UR contribute 33.3% and 40.0%, 28.8% and 38.3%, 29.6% and 36.4%, and 30.3% and 38.5% of the PN<sub>2.5</sub> EFs under the highway, rural road, urban road, and the whole trip, respectively. A major part of PN2.5 is clearly attributed to the fraction of particles <23 nm. Considering that the current PN limits are referred to solid >23 nm particles based on the electric mobility diameter [20,32], more attention should thus be paid to nanoparticles in the future limit. Relatively higher ratios of total <23 nm PN to PN<sub>2.5</sub> were observed for the vehicle without UR compared to that with UR, indicating the total <23 nm particles are more generated for the vehicle without UR that possesses normal urea injection [31].

Road Type	Urea State	Total <23 nm PN (×10 <sup>13</sup> #/km)	Solid >23 nm PN (×10 <sup>13</sup> #/km)	$PN_{2.5} ( imes 10^{13} \text{ #/km})$
	with UR	$1.4\pm0.1$	$2.8\pm0.1$	$4.2\pm0.1$
Highway	without UR	$2.2\pm0.4$	$3.4\pm0.4$	$5.5\pm0.8$
	DR (%)	36.9	16.9	24.7
	with UR	$1.7\pm0.2$	$4.2\pm0.9$	$5.9 \pm 1.1$
Rural	without UR	$3.1\pm0.5$	$5.2\pm0.8$	$8.1 \pm 1.3$
	DR (%)	45.8	19.2	27.3
	with UR	$2.9\pm0.2$	$6.9\pm2.3$	$9.8\pm2.1$
Urban	without UR	$7.9\pm0.1$	$13.8\pm0.3$	$21.7\pm0.5$
	DR (%)	63.1	50.4	55.0
	with UR	$1.7\pm0.1$	$4.0 \pm 0.8$	$5.6\pm0.8$
Whole trip	without UR	$3.0\pm0.7$	$4.8\pm1.0$	$7.8 \pm 1.7$
	DR (%)	43.3	18.4	27.8

Table 4. On-road PN EFs of the tested truck on different road types.

The decrease ratio (DR: %) in Table 4 was utilized to describe the reduction effect of the application of the UR on PN emissions. Lower total <23 nm and solid >23 nm PN emissions were observed for the situation with the application of the UR (Table 4), which is probably because much less NH<sub>3</sub> decomposed by urea over catalyst on the SCR can be achieved to contribute to the formation of particles. Meanwhile, the reduction effect on both total <23 nm and solid >23 nm PN emissions exhibited upward trends from the highway and rural roads to urban roads, which is opposite to the variation trend of the increasing effect on NOx emissions. This is likely because the NH<sub>3</sub> decomposed by urea can be more active in reducing NOx rather than forming particles in driving conditions with higher exhaust temperatures [19,33]. In particular, higher DRs occurred for the total <23 nm particles compared to solid >23 nm particles for those under various road types, which is consistent with the above findings, namely that the formation effect of NH<sub>3</sub> on total <23 nm particles is better than that on solid >23 nm particles. Furthermore, the reduction effect on total <23 nm particles is higher than that on solid >23 nm particles emitted under highways and

rural roads compared to urban roads. This phenomenon is probably related to the fact that ammonium nitrate formed by the reaction of NH<sub>3</sub> and NO<sub>2</sub> can tend to form more solid >23 nm particles in SCR catalyst pores under urban driving conditions with low exhaust temperature [34] compared to that under highway and rural roads.

#### 3.2.3. Effects on VSP-Bin PN Emission Rates

The average emission rates of total <23 nm and solid >23 nm PN of the truck with and without UR in various VSP and speed bins are demonstrated in Figure 4. The average VSP-bin total <23 nm and solid >23 nm PN emission rates of the vehicle without and with UR both generally exhibited obvious increasing trends in all speed ranges. Compared to the neglective differences in the VSP-bin peak emission rates among different speed ranges for the total <23 nm particles, the peak VSP-bin solid >23 nm PN emission rate of the low-speed range was higher than that in the other speed ranges. It was clear that the total <23 nm particles are more sensitive to the high engine load under high-speed driving conditions when compared to the solid >23 nm particles [31]. Moreover, compared to average solid >23 nm PN emission rates, the average total <23 nm PN emission rates without UR exhibit higher values than those with UR for all VSP and speed bins. Consequently, the usage of the UR resulted in obvious reductions in the average VSP-bin total <23 nm PN emission rates but fewer reductions in solid >23 nm PN emission rates. As shown in Figure 5, larger differences also occurred between the situation with and without UR for the <23 nm PN concentrations when compared to solid >23 nm PN concentrations. This may be explained by the presence of  $NH_3$  being more conducive to the formation of total <23 nm rather than solid >23 nm particles [35].



**Figure 4.** Comparison of average total <23 nm (**a**) and solid >23 nm (**b**) PN emission rates of different VSP-bins with and without the illegal application of urea regulator.



**Figure 5.** Variations in the PN size distribution under different VSP and speed bins both with and without the illegal application of urea regulator.

## 3.3. Variation in the Correlation between NOx and CO<sub>2</sub>

As described above, more distinguished effects of the UR can be obtained on NOx compared to PN emissions. Together with the easier access to obtain NOx emissions related to PN during the emission testing and other measurements such as the remote OBD [11], the variations in the correlation of CO<sub>2</sub> and NOx mass emission rates between the truck with and without UR under urban roads, rural roads, and the highway are thus analyzed. Figure 6 demonstrates the scatter plot diagram of  $CO_2$  (X-axis) and NOx (Y-axis) mass emission rates. The density distributions of emission rates and the fitting lines with intercept set to 0 under different road types with and without UR are also shown here. Clearly, most of the scatter for the truck with UR is located above those without UR, resulting in higher slopes for the fitting line with UR compared to that without UR. Obvious increasing differences in scatter distribution occurred between the situation with and without UR from urban roads, rural roads to the highway. This is mainly related to the increasing reduction effect of the SCR on NOx from urban roads and rural roads to the highway. The density distribution is thus more concentrated on the lower emission rates of NOx without UR compared to that with UR, especially for those emitted under the highway.



**Figure 6.** Scatter correlation diagrams of NOx instantaneous mass emission rates as a function of CO<sub>2</sub> for the vehicle with and without the UR under urban (**a**), rural (**b**), and highway (**c**) driving conditions.

Associated with the promoted efficiency in decreasing NOx of the SCR from urban roads and rural roads to the highway, the slopes of the fitting line without UR exhibited a distinguished downward trend. On the contrary, a slightly upward trend occurred for the slopes of the fitting lines with UR, which is attributed to the deficiency of the SCR without proper urea caused by the usage of the UR. Furthermore, the emission rates of NOx and  $CO_2$  for the vehicle with UR possessed good linear correlations under all road types, with the determination coefficient R<sup>2</sup> ranging from 0.8191 to 0.898. For the vehicle without UR, however, the determination coefficients R<sup>2</sup> exhibited an obvious downward trend from urban roads (0.8245) and rural roads (0.6931) to the highway (0.2544). This is probably related to the cumulatively poor positive responsiveness of NOx to  $CO_2$  caused by the increasing reduction efficiency of the SCR on NOx from urban roads and rural roads to the highway [36].

# 4. Conclusions

Real-world emission measurements on a China IV HDDT were conducted to investigate the characteristics of NOx and PN emissions under the situation both with and without the usage of UR. An obvious increased effect on NOx and a decreased effect on PN emissions were caused by UR. Specifically, the distribution of volumetric concentration was more concentrated at high and low concentrations for NOx and PN, respectively. From urban roads and rural roads to highways, an obvious rising increased effect on NOx while a decreasing decreased effect on PN emissions was clarified. Meanwhile, the peak VSP-bin NOx emission rates exhibited markedly increasing but decreasing trends from low- and medium- to the high-speed bin for those with UR and without UR, respectively. However, no similar findings can be observed for peak VSP-bin PN emission rates. Furthermore, the UR resulted in higher NOx emissions in-unit  $CO_2$  and linear correlations of NOx and  $CO_2$  emission rates. The slopes of the fitting line between NOx and  $CO_2$  emission rates exhibited a distinguished downward but slight upward trend from urban roads and rural roads to the highway for the situation without and with UR, respectively. These findings have potential employment prospects in the real-time identification of the malfunction of the SCR caused by the UR.

**Author Contributions:** Conceptualization, J.L. and F.Y.; methodology, Z.Y.; software, N.W.; validation, M.F., Z.Y. and H.M.; formal analysis, F.Y.; investigation, J.L.; resources, H.M.; data curation, Z.L.; writing—original draft preparation, J.L.; writing—review and editing, F.Y.; visualization, N.W.; supervision, F.Y.; project administration, M.F.; funding acquisition, F.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

**Data Availability Statement:** Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- 1. Winkler, S.L.; Anderson, J.E.; Garza, L.; Ruona, W.C.; Vogt, R.; Wallington, T.J. Vehicle criteria pollutant (PM, NOx, CO, HCs) emissions: How low should we go? *Npj Clim. Atmos. Sci.* **2018**, *1*, 26. [CrossRef]
- 2. Jing, B.; Wu, L.; Mao, H.; Gong, S.; He, J.; Zou, C.; Song, G.; Li, X.; Wu, Z. Development of a vehicle emission inventory with high temporal–spatial resolution based on NRT traffic data and its impact on air pollution in Beijing-Part 1: Development and evaluation of vehicle emission inventory. *Atmos. Chem. Phys.* **2016**, *16*, 3161–3170. [CrossRef]
- West, J.J.; Cohen, A.; Dentener, F.; Brunekreef, B.; Zhu, T.; Armstrong, B.; Bell, M.; Brauer, M.; Carmichael, G.; Costa, D.L.; et al. What We Breathe Impacts Our Health: Improving Understanding of the Link between Air Pollution and Health. *Environ. Sci. Technol.* 2016, 50, 4895–4904. [CrossRef] [PubMed]
- 4. Kelly, F.J.; Zhu, T. Transport solutions for cleaner air. Science 2016, 352, 934–936. [CrossRef]
- MEE. China Vehicle Environmental Management Annual Report of 2018; Ministry of Ecology and Environment of the People's Republic of China (MEE): Beijing, China, 2018.
- 6. MEE. China Mobile Source Environmental Management Annual Report 2021; Ministry of Ecology and Environment of the People's Republic of China (MEE): Beijing, China, 2021.
- Roberts, S.J.; Salawitch, R.J.; Wolfe, G.M.; Marvin, M.R.; Canty, T.P.; Allen, D.J.; Hall-Quinlan, D.L.; Krask, D.J.; Dickerson, R.R. Multidecadal trends in ozone chemistry in the Baltimore-Washington Region. *Atmos. Environ.* 2022, 285, 119239. [CrossRef]
- Cui, H.; Posada, F.; Lv, Z.; Shao, Z.; Yang, L.; Liu, H. Cost-Benefit Assessment of the China VI Emission Standard for New Heavy-Duty Vehicles. Available online: https://theicct.org/wp-content/uploads/2021/06/China\_VI\_cost\_benefit\_assessment\_ 20180910.pdf (accessed on 11 September 2018).
- 9. Zhang, S.; Wu, X.; Zheng, X.; Wen, Y.; Wu, Y. Mitigation potential of black carbon emissions from on-road vehicles in China. *Environ. Pollut.* **2021**, *278*, 116746. [CrossRef] [PubMed]
- 10. Wu, Y.; Zhang, S.; Hao, J.; Liu, H.; Wu, X.; Hu, J.; Walsh, M.P.; Wallington, T.J.; Zhang, K.M.; Stevanovic, S. On-road vehicle emissions and their control in China: A review and outlook. *Sci. Total Environ.* **2017**, *574*, 332–349. [CrossRef]
- Yang, L.; Zhang, S.; Wu, Y.; Chen, Q.; Niu, T.; Huang, X.; Zhang, S.; Zhang, L.; Zhou, Y.; Hao, J. Evaluating real-world CO2 and NOX emissions for public transit buses using a remote wireless on-board diagnostic (OBD) approach. *Environ. Pollut.* 2016, 218, 453–462. [CrossRef]

- Wang, J.; Wang, R.; Yin, H.; Wang, Y.; Wang, H.; He, C.; Liang, J.; He, D.; Yin, H.; He, K. Assessing heavy-duty vehicles (HDVs) on-road NOx emission in China from on-board diagnostics (OBD) remote report data. *Sci. Total Environ.* 2022, 846, 157209. [CrossRef]
- Zhang, S.; Zhao, P.; He, L.; Yang, Y.; Liu, B.; He, W.; Cheng, Y.; Liu, Y.; Liu, S.; Hu, Q.; et al. On-board monitoring (OBM) for heavy-duty vehicle emissions in China: Regulations, early-stage evaluation and policy recommendations. *Sci. Total Environ.* 2020, 731, 139045. [CrossRef]
- Raza, H.; Woo, S.; Kim, H. Investigation of an ammonium carbamate–based SCR system for NOx reduction in diesel engines under transient conditions. *Energy* 2022, 251, 123918. [CrossRef]
- 15. Lee, Y.; Lee, S.; Lee, S.; Choi, H.; Min, K. Characteristics of NOx emission of light-duty diesel vehicle with LNT and SCR system by season and RDE phase. *Sci. Total Environ.* **2021**, *782*, 146750. [CrossRef]
- Lemmetty, M.; Vehkamäki, H.; Virtanen, A.; Kulmala, M.; Keskinen, J. Homogeneous Ternary H2SO4-NH3-H2O Nucleation and Diesel Exhaust: A Classical Approach. *Aerosol Air Qual. Res.* 2007, 7, 489–499. [CrossRef]
- Thiruvengadam, A.; Besch, M.C.; Carder, D.K.; Oshinuga, A.; Gautam, M. Influence of Real-World Engine Load Conditions on Nanoparticle Emissions from a DPF and SCR Equipped Heavy-Duty Diesel Engine. *Environ. Sci. Technol.* 2012, 46, 1907–1913. [CrossRef]
- Guo, J.; Ge, Y.; Hao, L.; Tan, J.; Li, J.; Feng, X. On-road measurement of regulated pollutants from diesel and CNG buses with urea selective catalytic reduction systems. *Atmos. Environ.* 2014, *99*, 1–9. [CrossRef]
- Amanatidis, S.; Ntziachristos, L.; Giechaskiel, B.; Bergmann, A.; Samaras, Z. Impact of Selective Catalytic Reduction on Exhaust Particle Formation over Excess Ammonia Events. *Environ. Sci. Technol.* 2014, 48, 11527–11534. [CrossRef]
- Mamakos, A.; Schwelberger, M.; Fierz, M.; Giechaskiel, B. Effect of selective catalytic reduction on exhaust nonvolatile particle emissions of Euro VI heavy-duty compression ignition vehicles. *Aerosol Sci. Technol.* 2019, 53, 898–910. [CrossRef]
- Liu, S.; Wang, B.; Guo, Z.; Wang, B.; Zhang, Z.; Ma, X.; Chang, C.-T.; Wang, P.; He, X.; Sun, X.; et al. Experimental investigation of urea injection strategy for close-coupled SCR aftertreatment system to meet ultra-low NOx emission regulation. *Appl. Therm. Eng.* 2022, 205, 117994. [CrossRef]
- Salvachúa, V.; Checa, A. CITA-Applus+ Urea Emulator Emission Tampering. Available online: https://unece.org/sites/default/ files/2022-01/GRPE-85-31e.pdf (accessed on 13 January 2022).
- 23. Shen, X.; Lv, T.; Zhang, X.; Cao, X.; Li, X.; Wu, B.; Yao, X.; Shi, Y.; Zhou, Q.; Chen, X.; et al. Real-world emission characteristics of black carbon emitted by on-road China IV and China V diesel trucks. *Sci. Total Environ.* **2021**, *799*, 149435. [CrossRef]
- Wu, X.; Zhang, S.; Wu, Y.; Li, Z.; Zhou, Y.; Fu, L.; Hao, J. Real-world emissions and fuel consumption of diesel buses and trucks in Macao: From on-road measurement to policy implications. *Atmos. Environ.* 2015, 120, 393–403. [CrossRef]
- Järvinen, A.; Aitomaa, M.; Rostedt, A.; Keskinen, J.; Yli-Ojanperä, J. Calibration of the new electrical low pressure impactor (ELPI+). J. Aerosol Sci. 2014, 69, 150–159. [CrossRef]
- Dekati Ltd. The Dekati Engine Exhaust Diluter DEED. Available online: https://www.dekati.com/wp-content/uploads/dekati\_ deed\_brochure.pdf (accessed on 13 January 2021).
- 27. EPA. Exhaust Emission Rates for Heavy-Duty On-Road Vehicles in MOVES2014; EPA: Washington, DC, USA, 2015.
- Damma, D.; Ettireddy, P.; Reddy, B.; Smirniotis, P. A Review of Low Temperature NH<sub>3</sub>-SCR for Removal of NOx. *Catalysts* 2019, 9, 349. [CrossRef]
- 29. Musculus, M.P.B. Measurements of the Influence of Soot Radiation on In-Cylinder Temperatures and Exhaust NOx in a Heavy-Duty DI Diesel Engine. *SAE Trans.* 2005, 114, 845–866. [CrossRef]
- Herner, J.D.; Hu, S.; Robertson, W.H.; Huai, T.; Chang, M.-C.O.; Rieger, P.; Ayala, A. Effect of Advanced Aftertreatment for PM and NO<sub>x</sub> Reduction on Heavy-Duty Diesel Engine Ultrafine Particle Emissions. *Environ. Sci. Technol.* 2011, 45, 2413–2419. [CrossRef]
- 31. Saari, S.; Karjalainen, P.; Ntziachristos, L.; Pirjola, L.; Matilainen, P.; Keskinen, J.; Rönkkö, T. Exhaust particle and NOx emission performance of an SCR heavy duty truck operating in real-world conditions. *Atmos. Environ.* **2016**, *126*, 136–144. [CrossRef]
- 32. Giechaskiel, B.; Melas, A.; Martini, G.; Dilara, P.; Ntziachristos, L. Revisiting Total Particle Number Measurements for Vehicle Exhaust Regulations. *Atmosphere* **2022**, *13*, 155. [CrossRef]
- Ciardelli, C.; Nova, I.; Tronconi, E.; Chatterjee, D.; Bandl-Konrad, B.; Weibel, M.; Krutzsch, B. Reactivity of NO/NO2–NH3 SCR system for diesel exhaust aftertreatment: Identification of the reaction network as a function of temperature and NO2 feed content. *Appl. Catal. B Environ.* 2007, 70, 80–90. [CrossRef]
- Koebel, M.; Madia, G.; Elsener, M. Selective catalytic reduction of NO and NO2 at low temperatures. *Catal. Today* 2002, 73, 239–247. [CrossRef]
- 35. Shao, C.; Campuzano, F.; Zhai, Y.; Wang, H.; Zhang, W.; Sarathy, S.M. Effects of ammonia addition on soot formation in ethylene laminar premixed flames. *Combust. Flame* **2022**, *235*, 111698. [CrossRef]
- 36. Yang, Z.; Liu, Y.; Wu, L.; Martinet, S.; Zhang, Y.; Andre, M.; Mao, H. Real-world gaseous emission characteristics of Euro 6b light-duty gasoline- and diesel-fueled vehicles. *Transp. Res. Part D Transp. Environ.* **2020**, *78*, 102215. [CrossRef]