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High NO_2 Concentrations Measured by Passive Samplers in Czech Cities: Unresolved Aftermath of Dieselgate?

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Abstract: This work examines the effects of two problematic trends in diesel passenger car emissions—increasing NO_2/NO_x ratio by conversion of NO into NO_2 in catalysts and a disparity between the emission limit and the actual emissions in everyday driving—on ambient air quality in Prague. NO_2 concentrations were measured by 104 membrane-closed Palmes passive samplers at 65 locations in Prague in March–April and September–October of 2019. NO_2 concentrations measured by city stations during those periods were comparable with the average values during 2016–2019. The average measured NO_2 concentrations at the selected locations, after correcting for the 18.5% positive bias of samplers co-located with a monitoring station, were 36 $\mu g/m^3$ (range 16–69 $\mu g/m^3$, median 35 $\mu g/m^3$), with the EU annual limit of 40 $\mu g/m^3$ exceeded at 32% of locations. The NO_2 concentrations have correlated well (R^2 = 0.76) with the 2019 average daily vehicle counts, corrected for additional emissions due to uphill travel and intersections. In addition to expected "hot-spots" at busy intersections in the city center, new ones were identified, i.e., along a six-lane road V Holešovičkách. Comparison of data from six monitoring stations during 15 March–30 April 2020 travel restrictions with the same period in 2016–2019 revealed an overall reduction of NO_2 and even a larger reduction of NO. The spatial analysis of data from passive samplers and time analysis of data during the travel restrictions both demonstrate a consistent positive correlation between traffic intensity and NO_2 concentrations along/near the travel path. The slow pace of NO_2 reductions in Prague suggests that stricter vehicle NO_x emission limits, introduced in the last decade or two, have so far failed to sufficiently reduce the ambient NO_2 concentrations, and there is no clear sign of remedy of Dieselgate NO_x excess emissions.

Keywords: NO_2; passive sampler; Dieselgate; Prague; traffic volume; citizen science; air quality; public policy; health effects

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Highlights

- NO_2 measured by 104 passive samplers at 65 places in Prague, corrected mean 36 $\mu g/m^3$
- NO_2 increases with traffic intensity corrected for intersections and hills
- High NO_2/NO_x ratios and excess NO_x emissions from diesel cars a culprit
- Not much improvement after "Dieselgate"
- Reductions below 40 $\mu g/m^3$ suggested based on health evidence literature review

1. Introduction

Mobile sources, including on-road vehicles, remain to be one of the largest contributors to the air pollution in most metropolitan areas in Europe, with particulate matter and nitrogen oxides (NO_x, defined as a sum of nitric oxide NO and nitrogen dioxide NO_2) being of highest concern. Outdoor air pollution is now being considered one of the leading causes of premature death [1], with estimated tolls of approximately half a million premature deaths annually in the EU [2], and associated economic damage around 5% of HDP in Central Europe [3]. At the same time, the state-of-the art technology of the internal combustion engine has improved considerably over the last decades. Very low levels of sulfur and metals in the fuel have allowed the introduction of three-way catalysts on spark ignition engines, a common technology used throughout the U.S. over the last four decades with a somewhat delayed deployment in Europe, and the introduction of diesel particle filters on virtually all on-road diesel engines manufactured in the last decade. The emissions of nitrogen oxides, primarily NO, on engines operating with excess air remained a challenge, being ultimately resolved about a decade ago with selective catalytic reduction (SCR) systems on heavy-duty vehicles [4] and more recently also on light-duty vehicles.

In the EU, the concentrations of NO_2, deemed to be more detrimental to human health than NO, are limited and monitored in the ambient air. Overall, the concentrations of NO_2 have not been decreasing as fast as those of other key pollutants. In the Czech Republic, the concentrations of NO_2 at most air quality monitoring stations have been, according to the data in [5], decreasing by on the order of 1% a year over the last two decades. A gradual decrease of NO_2 concentrations in the overall atmosphere above the Czech Republic over the last decade has been also reported from remote sensing satellite measurements [6].

NO_2 in ambient air originates both from direct (primary) emissions and from gradual conversion of NO into NO_2 [7]. While the total emissions of NO_x have been gradually decreasing, there is no apparent trend of a decrease in NO_2 primary emissions over the last 15 years [6]. One of the culprits of high primary NO_2 emissions are diesel vehicles, which have been, over the last two decades, equipped with oxidation catalysts, which convert a considerable portion of NO into NO_2. In the U.S., average NO_2/NO_x ratio in vehicle exhaust (all vehicles, including predominantly gasoline cars and light trucks and predominantly diesel heavy trucks) was 5.3% [8], compared to approximately 15% in Europe [9].

This paper explores a hypothesis that the observed decrease in NO_2 concentrations falls short of that expected based on order-of-magnitude decrease in vehicle NO_x emissions limits and that non-compliant diesel cars could substantially contribute to this shortfall. The underlying aspects of NO_x emissions and the adverse health effects of NO_2 are summarized. The results of a monitoring NO_2 with passive samplers are reported and discussed in light of these findings. As an additional insight, the effects of coronavirus related restrictions on NO and NO_2 concentrations in Prague are reported and discussed.

2. Review of Trends and Shortcomings in NO_2 and NO_x Emissions from Vehicles

Nitrogen oxide (NO) is formed in combustion processes from atmospheric nitrogen and oxygen at high temperatures [10,11], which are generally associated both with efficient combustion and with high thermal efficiency of the engine. Subsequent oxidation of NO in the atmosphere yields primarily nitrogen dioxide (NO_2), a brownish irritant gas. Other oxides of nitrogen—N_2O_2, N_2O_3, N_2O_4, N_2O_5—are generated in small concentrations, are unstable and short-lived in the atmosphere. The oxides of nitrogen are summarily referred to as NO_x, although there is no precise definition. Often, NO_x is evaluated as the sum of NO and NO_2. Technically, the sum of NO_x also includes nitrous oxide (N_2O), which is, however, not hazardous to human health, but is a potent greenhouse. NOx leads to the formation of nitrous acid (HNO_2) [12,13], nitric acid (HNO_3) and a variety of salts such as ammonium nitrate, present in the atmosphere as particulate matter [14]. Photodissociation of NO_2 under the presence of sunlight produces NO and atomic oxygen, which reacts with molecular oxygen to form ozone [15], a highly reactive compound generally harmful to human health, organisms and plants. NO_x and ground-level (tropospheric) ozone are, together with particulate matter, the principal part of urban air pollution.

On spark ignition engines, CO and VOC, principally a product of incomplete oxidation of fuel and to a lesser extent engine lubricating oil, and NO_x have been successfully abated by the combination of three-way catalysts [16] and by maintaining stoichiometric air–fuel ratio through closed-loop control of the quantity of fuel injected [17]. This technology has proven to be remarkably efficient.

On diesel engines, the emissions of NO_x have been, at first, controlled through delayed combustion timing and exhaust gas recirculation, both associated with a slight fuel penalty, and at a later time, with NO_x storage and reduction catalysts and selective reduction catalysts (SCR). The reduction of NO_x has historically come at an expense of both capital and operating costs, with operating costs including either fuel (notably on older vehicles using delayed combustion, exhaust gas recirculation, NO_x storage and reduction catalysts) or a reducing agent used in SCR (mostly aqueous solution of urea, known as diesel exhaust fluid or "AdBlue"). These costs have motivated, over the last few decades, many manufacturers and vehicle users to circumvent NO_x reduction efforts, as the savings were realized by them directly, while considerably larger overall damage to human health was born by the society, a problem known as the Tragedy of the Commons [18]. A widespread practice of dual engine mapping in the U.S. in the 1990s [19,20] has led to the gradual extension of vehicle emissions limits to ordinary on-road operation first of heavy-duty and later of light-duty vehicles [21–23]. In the heavy-duty vehicle engine sector, many recent studies now show that on-road NO_x emissions of newer heavy-duty vehicles have been successfully reduced by an order of magnitude except for low-load operation typical for congested urban areas. Quiros et al. [24] reports NO_x emissions of 2013 and 2014 model year heavy trucks of 0.36 g/km during motorway operation in California. Jiang et al. [25] reports, for similar conditions, 0.3 g/km NO_x during extraurban and motorway operation. Grigoratos et al. [26] reports NO_x emissions during motorway operation in Europe of 0.07, 0.08, 0.17 and 0.24 g/kWh for four trucks and 0.80 g/kWh for a bus. Giechaskiel et al. [22] reports NO_x emissions of a garbage collection truck of less than 0.4 g/kWh during extraurban operation (note: for heavy vehicles, emissions per kWh roughly correspond to emissions per km).

Unfortunately, this has not been the case with light-duty vehicles with diesel engines, highly prevalent in Europe, where they account for several tens of percent of vehicle registration and in Prague, for about two thirds of vehicles counted on the road [27]. Large portion of European automobile diesel engines produced over the last one to two decades have been reported to emit substantially, often by an order of magnitude, more NO_x on the road than during the type approval test [28–32]. Weiss et al. [29] reports on-road NOx emissions factors 0.76 ± 0.12 g/km for Euro 4, 0.71 ± 0.30 g/km for Euro 5 and 0.21 ± 0.09 for Euro 6. In a more recent study by Suarez-Bertoa et al. [23], NO_x emissions from Euro 6 diesel cars varied substantially from mid tens to mid hundreds of milligrams of NO_x per kilometer, with a median value of about 0.2 g/km NO_x during the city-motorway test.

At the same time, on nearly all light-vehicle diesel engines of the last decade or so, oxidation catalysts are used to convert NO into NO_2, as higher concentrations of NO_2, around 10%, are beneficial both for the combustion of soot in DPF and for the "fast" reduction of NO_x in SCR catalysts. As a result, NO_2 from newer engines accounts for 10% of NO_x [33,34]. On passenger cars and light-duty trucks, NO_2/NO_x ratios of around 10–15% up to Euro 3 and 25–30% for Euro 4 and 5 were found in a London remote sensing study [35]. In the U.S., NO_2/NO_x ratio from heavy duty diesel trucks have doubled from around 7% in 2010 (average of trucks passing on the road in a given year, not a model year of the vehicles) to around 15% in 2018 [36]. This increase, however, did not result in an absolute increase in NO_2 emissions, as total NOx emissions have decreased dramatically due to the widespread use of SCR catalysts. According to Preble [36], "Fleet-average NO_2 emission rates remained about the same, despite the intentional oxidation of engine-out NO to NO_2 in DPF systems, due to the effectiveness of SCR systems in reducing NO_x emissions and mitigating the DPF-related increase in primary NO_2 emissions".

In Europe, NO_x emissions from diesel cars have not, however, decreased in proportion to the decreasing emissions limits. A recent on-road study in Prague reports the mean emissions of Euro 5 and 6 diesel cars and vans of over 0.1 g/km NO_2 and over 0.5 g/km NO_x [37], while a recent study of one of the most common diesel cars (Euro 6) reported about 0.15 g/km over WLTC cycle, and about 0.4 g/km over the Artemis driving cycle [38], which is more than the 0.08 g/km Euro 6 limit for total NO_x (with which the vehicle reasonably complied over the NEDC cycle).

The presumption of the regulators that increased the NO_2/NO_x ratio after the oxidation catalyst and before the DPF, highly beneficial both for DPF and SCR operation, will be mitigated by the rather high efficiency of the NO_x aftertreatment, envisioned in both U.S. EPA and EU emissions standards, which has been compromised by intentional acts resulting in diminished, or even zero, efficiency of the NO_x aftertreatment. Examples of such acts include dual-mapping of the engines by the manufacturers (a prime example of which is "Dieselgate") and disabling of the SCR (and emulating its proper functioning to the on-board diagnostics by "SCR emulators") by vehicle operators. Under such conditions, relatively high amounts of NO_2, intended to be reduced in NO_x aftertreatment, are emitted out of the tailpipe. Logically, this results in very high, and much higher than intended, primary emissions of NO_2 in the streets. This finding is consistent with the rather slow decrease in NO_2 concentrations.

3. Review of the Impact of NO_2 to Central Nervous System in Children and Adults

The first experimental data were obtained several decades ago, indicating that air pollution may induce behavioral changes. Singh [39] studied the effect of NO_2 exposure on pregnant mice, exposed during gestation day 7–18. Prenatal exposure significantly altered the righting reflex and aerial righting score. These results suggest that maternal NO_2 exposure produce deficits in the functional capability of the offspring.

Wang et al. [40] was the first one, who studied the impact of NO_2 exposure to children's neurobehavioral changes. They studied this effect in the year 2005 on two groups of children (A N = 431, B N = 430) in the age of 8–10 years using neurobehavioral testing. Group A was exposed to 7 μg NO_2/m^3, group B to 36 μg NO_2/m^3. Children from the polluted area showed poor performance in all tests: visual simple reaction time, continuous performance, digit symbol, pursuit aiming and sign register, This study found a significant relationship between chronic low-level traffic related air pollution and neurobehavioral function in exposed children.

Guxens et al. [41] analyzed the association between prenatal exposure, diet and infant mental development in four regions in Spain, in 1889 children, who were exposed to 29.0 $\pm$ 11.2 μg NO_2/m^3 (20.1–36.8). Infant mental development was evaluated at 14 months by Bailey Scales of Mental Development. Exposure to NO_2 did not show a significant association with mental development. Inverse association was observed in infants whose mothers reported low intake of fruit/vegetables during pregnancy ($-$4.13 ($-$7.06, $-$1.21)). This study suggests that antioxidants in fruits and vegetables during pregnancy may modulate an adverse effect of NO_2 on infants' mental development.

Kim et al. [42] investigated the association between maternal exposure to NO_2 of 49.4 μg/m^3 (25.9–84.8) and neurodevelopment in children in Korea (mental development index (MDI) and the psychomotor development index (PDI) by Bailey scales of mental development) at ages 6, 12 and 24 months. This study used 455–371 children. NO_2 exposure impaired psychomotor development ($\beta = -1.30$; $p = 0.05$). At 6 months NO_2 affected MDI ($\beta = -3.12$; $p < 0.001$) and PDI ($\beta = -3.01$; $p < 0.001$). These data suggest that exposure to NO_2 may delay neurodevelopment in early childhood.

A similar study was organized in Spain on 438 mother-child pairs by Lertxundi et al. [43] at 15 months of age, using the Bailey scales of mental development. A 1 μg NO_2/m^3 increase during pregnancy decreased the mental score ($\beta = -0.29$; 90% CI: -0.47; -0.11). Prenatal residential exposure to NO_2 adversely affects infant motor and cognitive development.

A prospective cohort study was conducted with 2715 children aged 7–10 years in Barcelona, Spain, as a part of the BREATHE project (brain development and air pollution ultrafine particles in school children [44]). Children were tested every 3 months with a computerized test. Cognitive development was assessed with the n-back and the attentional network test as working memory and inattentiveness. NO_2 exposure was completed in the outdoors in a low traffic region 40.5 ± 9.6 μg/m^3 and high traffic region 56.1 ± 11.5 μg/m^3. Children attending schools with higher NO_2 pollution had an 11.5% (95% CI 8.9%–12.5%) slower working memory and slower growth in all cognitive measurements, which means a smaller improvement in cognitive development.

Pujol et al. [45] selected from this cohort 263 children, aged 8–12 years, for magnetic resonance investigation (MRI) to analyze brain volumes, tissue composition, myelination, cortical thickness, neural tract architecture, membrane metabolites and functional connectivity. Outdoor NO_2 exposure was 46.8 ± 12.0 μg/m^3/year and indoor NO_2 exposure was 29.4 ± 11.7 μg/m^3/year. Higher NO_2 exposure was associated with slower brain maturation with changes specifically concerning the functional domain.

Forns et al. [46] evaluated 2897 children from the Barcelona cohort within the BREATHE project. NO_2 exposure in schools was 29.82 μg/m^3 (11.47–65.65) and outdoor was 48.46 μg/m^3 (25.92–84.55). Behavioral development was assessed using the strengths and difficulties questionnaire (SDQ), which was filled out by parents. NO_2 exposure was positively associated with SDQ total difficulties scores, suggesting more frequent behavioral problems. This study was understood as the first one to evaluate the impact of air pollution on behavioral development in schoolchildren using both indoor and outdoor air pollution levels measured at schools. NO_2 outdoor levels (IQR = 22.26 μg/m^3) significantly increased total difficulties score (1.07, 95% CI: 1.01, 1.14, $p < 0.05$). NO_2 exposure at school is associated with worse general behavioral development in schoolchildren.

Min and Min [47] studied in Korea 8936 children born in the year 2002 and followed them for the next 10 years, investigating the relationship between exposure to NO_2 and attention-deficit hyperactive disorder (ADHD). They diagnosed 313 children with ADHD. The hazard ratio (HR) associated with the increase in 1 μg of the NO_2/m^3 was 1.03 (95% CI: 1.02–1.04). Comparing infants with lowest tertile of NO_2 exposure with the highest tertile of NO_2, HR = 2.10 (95% CI: 1.54–2.85), exposure had a 2 fold increased risk of ADHD. The study showed a significant association between exposure to NO_2 and the incidence of ADHD in children.

Sentis et al. [48] evaluated prenatal and postnatal exposure to NO_2 and attentional function in children at 4–5 years of age in four regions of Spain (N = 1298). The attentional function was evaluated by the Conners kiddie continuous performance test (K-CPT). The prenatal NO_2 level was 31.1 μg/m^3 (18.4–37.9). Higher exposure to prenatal levels of NO_2 was associated with a 1.12 ms (95% CI; 0.22, 2.02) increase in hit reaction time and 6% increase in the number of emission errors (95% CI: 1.01, 1.11) per 10 ug/m^3 increase in prenatal NO_2. Higher exposure to NO_2 during pregnancy is associated with impaired attentional function, especially increased inattentiveness in children aged 4–5 years. This reduced attentional function in population could lead to poor educational indicators. It seems to be important that this effect was observed with NO_2 concentrations lower than EU standard 40 μg/m^3.

Sunyer et al. [49] followed in 2012–2013 2687 school children from Barcelona, assessing children´s attention process 4 times every three months, using the attention network test (ANT). NO_2 indoor pollution was 30.09 ± 9.51 μg/m^3 and ambient air pollution was 37.75 ± 18.41 μg/m^3. Daily ambient levels were negatively associated with all attention processes (children in the bottom quartile of daily exposure to NO_2 had a 14.8 ms (95% CI: 11.2, 18.4) faster response time than those in the top quartile, which corresponds to a 1.1 month delay (95% CI: 0.84, 1.37) in natural development). Short-term exposure to NO_2 is associated with potential harmful effects on neurodevelopment.

Forns et al. [50] examined after 3.5 years the cohort of children from Barcelona (N = 1439), whose cognitive development was evaluated 4 times in the years 2012/2913 [43].

Working memory was estimated by a computerized n-back test. Exposure to NO_2 was related to the slower development of working memory (β = −4.22, 95% CI: −6.22, −2.22). These reductions corresponded to a −20% (95% CI: −30.1, −10.7) change in annual working memory development associated with one interquartile range increase in outdoor NO_2. Forns et al. [50] observed a persistent negative association between NO_2 levels at school and cognitive development over a course of 3.5 years. Therefore, they suggested that highly exposed children might face obstacles to fully achieve their academic goals.

Vert et al. [51] analyzed association between exposure to NO_2 and mental disorders on 958 residents from Barcelona (45–74 years old). Long-term residential exposure (period 2009–2014) was related to patients' self-reported history of anxiety and depression disorders. NO_2 exposure corresponded to 57.3 μg/m^3 (50.7–62.7). NO_2 increased the odd ratio for depression of 2.00 (95% CI: 1.37, 2.93) for each 10 μg NO_2/m^3 increase. The study shows that long-term exposure to NO_2 may increase the incidence of depression.

Alemany et al. [52] analyzed on the group of children from the BREATHE project (*N* = 1667 at the age of 11 years), if there is any association between traffic-related air pollution and the ε4 allele of the apolipoprotein E gene, which is understood as a genetic risk factor for Alzheimer´s disease. NO_2 exposure at the home address was 54.25 ± 18.40 μg/m μg/m^3 and at schools was 47.74 ± 12.95 μg/m^3. NO_2 exposure increased behavioral problems scores (characterized by SDQ) in ε4 carriers (*N* = 366) vs. non-carriers (*N* = 1223) 1.14 (95% CI: 1.04, 1.26) vs. 1.02 (95% CI: 0.95, 1.10, *p* = 0.04) and was associated with smaller caudate volume in ε4 carriers (*N* = 37) vs. non-carriers (*N* = 126) −737.9 (95% CI: −1201.3, −274.5) vs. −157.6 (95% CI: −388.8, 73.6, *p* = 0.03). Annual average NO_2 concentrations in children´s schools were associated with smaller caudate volume and higher behavior problem scores among APOE ε4 allele carriers. It is possible that ε4 carriers are more vulnerable to neuroinflammatory and oxidative stress induced by air pollution exposure.

Carey et al. [53] investigated the incidence of dementia to residential level of NO_2 in London. Among 130,978 adults aged 50–79 years was, in the period 2005–2013, 2181 subjects diagnosed with dementia (39% Alzheimer´s disease and 29% vascular dementia). The average annual concentration of NO_2 was 37.1 ± 5.7 μg/m^3. Higher risk of Alzheimer´s disease was observed in subjects exposed to the highest concentrations of NO_2 (>41.5 μg/m^3) vs. subjects with the lowest concentrations of NO_2 (<31.9 μg/m^3) (HR = 1.40, 95% CI 1.12–1.74). These associations were more consistent for Alzheimer´s disease than vascular dementia. Study found evidence of a positive association between residential level of NO_2 across London and being diagnosed with dementia.

Roberts et al. [54] explored the effect of NO_2 exposure to mental health problems in children in London, U.K. (*N* = 284). Symptoms of anxiety, depression, conduct disorder and ADHD were assessed at ages 12 and 18. NO_2 concentration in the year 2007 was 37.9 ± 5.5 μg/m^3 (IQR 34.1–41.7). They did not observe any association between NO_2 exposure in childhood and mental health problems at age 12. However, they detected association between NO_2 exposure and subsequent development of symptoms and clinically diagnosable depression and conduct disorders at age 18. They demonstrated that NO_2 exposure at age 12 years was significantly associated with major depressive disorder at age 18.

Prenatal exposure to NO_2 and sex dependent infant cognitive and motor development was analyzed by Lertxundi et al. [55] in children at 4–6 years of age, in four regions in Spain (*N* = 1119). Infant neuropsychological development was assessed by McCarthy scales: verbal, perceptive-manipulative, numeric, general cognitive, memory and motor. NO_2 exposure during pregnancy was from 18.7 ± 6.1 to 41.8 ± 10.7 μg/m^3. The majority of cognitive domains were negative for NO_2, associations were more negative for boys, statistically significant for memory, global cognition and verbal. These findings indicate a greater vulnerability of boys in domains related to memory, verbal and general cognition.

Jorcano et al. [56] assessed association between NO_2 and depressive and anxiety symptoms, and aggressive symptoms in children of 7–11 years, related to their prenatal and postnatal exposure. Data were analyzed in 13,182 children from eight European population-based cohorts. Prenatal NO_2 levels ranged from 15.9 to 43.5 µg/m^3, postnatal levels ranged from 14.0 to 43.5 µg/m^3. A total of 1108 (8.4%) and 870 (6.6%) children were classified as having depressive and anxiety symptoms, and with aggressive symptoms. Obtained results suggest that prenatal and postnatal exposure to NO_2 is not associated with depressive and anxiety symptoms or aggressive symptoms in children of 7–11 years old.

Loftus et al. [57] used the mother–child cohort from the CANDLE study and analyzed the impact of prenatal NO_2 exposure (22.3 ± 7.1 µg/m^3) and postnatal exposure (16.2 ± 4.7 µg/m^3) on childhood behavior (N = 975). In the sample 64% were African American, 53% had a household annual income below USD 35,000 and the child's age was 4.3 years. Mothers completed the child behavior checklist, a measure of problem behaviors in the past two weeks. The 4 µg/m^3 higher prenatal NO_2 was positively associated with externalizing behavior (6%, 95% CI: 1, 11%) and the effect of postnatal exposure was stronger (8%, 95% CI: 0, 16%). Prenatal NO_2 exposure was also associated with significant internalizing and externalizing behaviors. NO_2 exposure is positively associated with child behavior problems and African American and low SES children may be more susceptible.

Kulick et al. [58] examined in 5330 participants from the Northern Manhattan area of New York City the effect of long-term exposure to NO_2 (annual estimates 57.4 ± 22.1 µg/m^3) and $PM_{2.5}$ (annual estimates 13.1 ± 4.8 µg/m^3), predominantly in women, with a median age of 75.2 (±6.46) years. A + IQR increase of residential NO_2 was predictive of a 22.SD (95% CI, 0.30, −0.14) low global cognitive score at baseline and a more rapid decline (−0.06 SD; 95% CI −0.08, −0.04) in global cognitive function between biennial visits.

Erikson et al. [59] studied the association between NO_2 exposure and total gray matter and total white matter volumes in adults, using sample from UK Biobank. Participants were recruited from 2006 to 2010, a subset with magnetic-resonance brain imaging (MRI) included 18,292 participants, with an average age of 62 (44–80) and NO_2 levels were 25.61 ± 6.86 µg/m^3. The mean total gray-matter volume was 708,111 mm^3 (±47,940), the mean total white-matter volume was 708,111 mm^3 (±40,696). The total gray-matter volume was inversely associated with NO_2 (b = −103, p < 0.01). The effect of NO_2 on gray-matter volume was more pronounced in females (b = 161, p < 0.05). Obtained findings suggest that NO_2 concentrations lower than EU standard could be associated with reduced total gray-matter.

All reviewed studies indicate a significant health risk of NO_2 exposure at concentrations lower than the EU annual limit of 40 µg/m^3:

- Prenatal exposure impaired attentional function at the age of 4–5 years;
- Induce neurobehavioral changes in children at the age of 8–10 years;
- Affect attention process in children aged 8–12 years and induced changes are persistent for another 3.5 years;
- Increase major depressive disorder at age 18;
- Increase the incidence of dementia;
- Exposure to NO_2 is associated with reduced total gray-matter.

The overall evidence presented in the mentioned studies suggests that attainment of the current EU annual limit for NO_2 of 40 µg/m^3 may not be sufficient for the protection of human health and further reductions of NO_2 concentrations would be beneficial and should be considered. In Switzerland, the current limit for the annual average of NO_2 is 30 µg/m^3.

4. Measurement of NO_2 in Prague by Passive Samplers

To build up on this hypothesis, the measurements of NO_2 concentrations at various locations by passive samplers are examined. Some of the results were presented by Deutsche Umwelthilfe [60] as preliminary data; in this study, the results from Prague were examined in a greater detail.

For passive monitoring, membrane-closed Palmes tube [61] passive samplers (Passam, Switzerland [62]) were used. Several hundreds of samplers were placed at selected locations in the Czech Republic, out of which 65 were in Prague, during spring and fall of 2019 (46 and 58 samplers, respectively, a total of 104 samplers), each time for a period of approximately one month. The placement of the tubes generally followed the requirements set in the EU air quality directive (2008/50)—placement away from buildings at a breathing height 1.5–4 m, away from larger obstructions, and for traffic sites, within 10 m of curbside and, in most cases, over 25 m from intersections. In some cases, the samplers were placed closer to intersections, and in some cases, the samplers were placed in less conspicuous places such as behind a traffic sign (see photo in Figure 1), to reduce the chances of tampering. The expanded uncertainty (95% confidence) of the measurement given by the manufacturer is 18.3% for a concentration range 20–40 μg/m^3 [62]. The location of samplers is shown on an overview map in Figure 1. The same map also shows the locations of the national air quality monitoring stations referred to in this study.

Figure 1. Locations of the passive samplers and air quality monitoring stations used for comparison in this study. Photo of a sampler is shown in the upper right corner. (Map source: www.mapy.cz (accessed on 18 May 2021), © Seznam.cz, a.s., used with permission).

The measured concentrations are given in Table 1. For the spring campaign, the dates of the sampling are listed in the “spring measurement period” column, while for the fall campaign, a value is given when a measurement has taken place during the three sampling periods, as some locations were sampled twice. The spring, fall and overall average concentrations, divided by a correction factor of 1.185 (will be explained later in the manuscript) are given. For each location, the average daily vehicle traffic counts reported by the City of Prague Highway Department for 2019 [63] are reported. This table also reports vehicle counts adjusted for additional emissions due to inclines and intersections, these adjustments are discussed later in the manuscript.

Table 1. Measured NO_2 concentrations and average daily vehicle counts.

NO_2 Measurements by Passive Samplers	Sprimg Measurement Period	Concentration as Analyzed [μg/m^3]				Adjusted (div 1.185) Concentrations			Traffic Vehicles/Day			Hill Climb	Inter-Section	>6 tons Excl. Zone
Location		March–April	30 August–29 September	7 September–30 October	29 September–30 October	Spring	Fall	Average	Total Vehicles	Heavy Vehicles	Adjusted			
31 Budějovická	9 March–6 April	34				28		28						1
32 třída 5. května 39	9 March–6 April	43			41	36	35	35	73,818	2200	110,727	50%		1
33 Na Veselí	9 March–6 April	49			41	41	35	38	15,500	400	31,000	100%		1
34 Sokolská/Ječná	9 March–6 April	78	70		63	66	56	61	56,000	1700	280,000	100%	100%	1
35 Ječná/Štěpánská	9 March–6 April	64		63		54	53	53	27,600	700	138,000	100%	100%	1
36 Jugoslávských partyzánů 27	9 March–6 April	35				29		29	16,723	800	16,723			
37 Na pískách/Evropská	9 March–6 April	52		56		44	48	46	40,600	1700	162,400		100%	
38 Kafkova/Svatovítská	9 March–6 April	46		46		39	39	39	26,101	1000	104,404		100%	
39 Svatovítská/tunel	9 March–6 April	31		34		26	29	27	36,901	1000	36,901			
40 Na Ořechovce	9 March–6 April	45				38		38	12,800	400	12,800			
41 Dejvice train station	9 March–6 April	73		59		62	50	56	29,200	1400	131,400	50%	100%	1
42 Hradčanská (metro station)	9 March–6 April	34		36		29	30	30	18,409	1100	18,409			1
43 Veletržní/Sochařská	9 March–6 April	50		47		43	40	41	22,100	600	99,450	50%	100%	1
44 Janovského/Veletržní	9 March–6 April	41		34		34	29	31	19,400	400	77,600		100%	1
45 Křížovnická	9 March–6 April	40				34		34	21,000	500	21,000			1
46 Vinohradská/Flora	9 March–6 April	34			37	29	31	30	26,400	600	26,400			
47 Flora-mall (bus stop)	9 March–6 April	43			35	36	30	33	11,312	200	45,248		100%	
48 Bělocerkevská (bus stup)	9 March–6 April	51			46	43	39	41	26,500	1000	132,500	100%	100%	
49 Vršovická (Slavia tram stop)	9 March–6 April	33			36	28	31	29	13,900	600	55,600		100%	
52 Rumunská/Sokolská	9 March–6 April	53				45		45	43,100	1300	129,300	50%	50%	1
120 Severni Spořilov podchod	13 March–24 April	45				38		38	48,900	7200	73,350	50%		
121 Chodov/Dálnice	13 March–24 April	55				46		46	118,100	15,600	177,150	50%		
122 Zenklova/Na Korábě	13 March–24 April	39			30	33	25	29	13,000	400	13,000			
123 Vychovatelna (bus)	13 March–24 April	67			49	57	41	49	109,300	4700	163,950	50%		
124 Rokoska (podchod)	13 March–24 April	64			53	54	45	49	88,561	4200	132,842	50%		
125 V Holešovičkách 8/10	13 March–24 April	51			45	43	38	40	88,561	4200	132,842	50%		
126 Hotel Pawllovia	13 March–24 April	40			43	34	36	35	88,561	4200	88,561			
127 main train station	13 March–24 April	42	51			35	43	39	85,053	200	85,053			1
128 Hrusická 6 (balcony)	13 March–24 April	21				18		18	0	0	0			

Table 1. *Cont.*

NO_2 Measurements by Passive Samplers	Sprimg Measurement Period	Concentration as Analyzed [μg/m^3]				Adjusted (div 1.185) Concentrations			Traffic Vehicles/Day			Hill Climb	Inter-Section	>6 tons Excl. Zone
Location		March–April	30 August–29 September	7 September–30 October	29 September–30 October	Spring	Fall	Average	Total Vehicles	Heavy Vehicles	Adjusted			
129 hlavni 25 (balcony)	13 March–24 April	29				25		25	8000	200	8,000			
130 Havni/most	13 March–24 April	37				31		31	50,487	7400	75,731	50%		
181 Kotevní 2	19 March–24 April	32				27		27	26,500	600	26,500			1
182 Strakonická 21/23	19 March–24 April	41				35		35	54,753	3300	54,753			1
183 Svornosti 19a	19 March–24 April	48				41		41	11,800	300	11,800			1
184 Zborovská 3	19 March–24 April	48	44		44	41	37	39	14,500	300	58,000		100%	1
185 V Botanice 4 (regional government)	19 March–24 April	56	49		63	47	47	47	25,028	500	100,112		100%	1
186 V Botanice (bank)	19 March–24 April	43			44	37	37	37	22,000	500	88,000		100%	1
187 Plzeňská 14, Hotel IBIS	19 March–24 April	49			42	41	35	38	32,700	700	130,800		100%	
188 Radlická 14/Anděl	19 March–24 April	48			48	40	41	41	25,030	600	100,120		100%	
189 Ostrovského	19 March–24 April	43	41			36	34	35	23,191	500	92,762		100%	
190 Billa Karlin	19 March–24 April	32		28		27	24	25						
191 Pobřežní (bussiness center)	19 March–24 April	43		40		37	33	35	31,200	1200	31,200			
192 Pobřežní (monitoring stattion)	19 March–24 April	38		30		32	26	29	31,200	1200	31,200			
193 Negreliho viadukt	19 March–24 April	33		39		28	33	30	13,335	800	13,335			
194 Florenc (bus stop)	19 March–24 April	46		42		39	36	37	14,612	800	58,448		100%	
195 Nám. Republiky (Kotva)	19 March–24 April	47				40		40	8300	300	33,200		100%	1
Mezibranská 3	none		84		79		69	69	59,645	1800	298,225	100%	100%	1
Sokolská/Ječná, Prague	none		74		63		58	58	55,445	1700	277,225	100%	100%	1
Rumunská/Legerova, Prague	none		62		52		48	48	45,452	1300	181,808		100%	1
Bubenská, Prague	none			48			40	40	28,300	800	113,200		100%	
Vysočanská, Prague	none			26			22	22	15,700	400	15,700			
Vysočanská (ČHMÚ), Prague	none			37			31	31	37,035	1600	148,140		100%	

Table 1. *Cont.*

NO$_2$ Measurements by Passive Samplers	Sprimg Measurement Period	Concentration as Analyzed [μg/m^3]				Adjusted (div 1.185) Concentrations			Traffic Vehicles/Day			Hill Climb	Inter-Section	>6 tons Excl. Zone
Location		March–April	30 August–29 September	7 September–30 October	29 September–30 October	Spring	Fall	Average	Total Vehicles	Heavy Vehicles	Adjusted			
Thámova/Sokolovská, Prague	none			28			24	24						
Radlická (ČSOB), Prague	none			38			32	32						
Radlická (Kotelna Park), Prague	none			33			28	28						
Resslova 1/3, Prague	none			52			44	44	33,027	700	148,622	50%	100%	
Spořilov 1, Prague	none				51		43	43						
Spořilov 2, Prague	none				34		28	28						
Boční/Jihovýchodní VII, Prague	none				28		24	24						
Pankrác 1 BAUHAUS, Prague	none				37		31	31					100%	
Pankrác 2 Doudlebská, Prague	none				29		25	25					100%	
Pankrác 3 viadukt, Prague	none				32		27	27					100%	
Pankrác 4 Hvězdova 35, Prague	none				31		26	26					100%	
Radlická/Klicperova, Prague	none				48		41	41	25,030	500	100,120		100%	
Suchdol AV ČR, Prague	none				20		17	17	0	0	0			
Suchdol AV ČR, Prague	none				19		16	16	0	0	0			

4.1. Validation by Comparison with the Air Quality Monitoring Network

According to [64], passive diffusion tubes for measuring NO_2 concentrations in air were originally developed in the late 1970s for personal monitoring. They have been widely used in Europe for spatial and temporal measurement of NO_2 concentrations. The method has been found to be cheap, simple, and "provides concentration data in most circumstances that are sufficiently accurate for assessing exposure and compliance with Air Quality criteria" [64]. Reporting on a series of comparison tests, Buzica et al. [65] have concluded that "In the case of NO_2, all the results of the laboratory and field experiments respected the requirements necessary for the demonstration of equivalence" and that the MCPT are equivalent to the reference methods for assessment of NO_2. Passive diffusion tubes were reported to show a positive bias when sampling close to sources of NO, such as roadside or street canyons [64]. At the same time, prolonged (several weeks) sampling periods were reported to lead to negative bias [64]. A review done by the Joint Research Center of the European Commission [66], done in part to assess the feasibility of using the samplers for the long-term monitoring of nitrogen dioxide, with the particular aim of checking compliance with the European Union annual limit value of 40 μg/m^3, citing a range of previous studies, reports that the "precision of the sampler showed that it is usually better than 5% when using a barrier or shelter to reduce effects of wind-induced turbulence" and that "the relative expanded uncertainty of individual results was estimated to be 32% for worst-case conditions", with lower values, generally <25%, obtained, for example, by parallel measurements with a reference method, by direct approaches, concluding that overall, "the Palmes tube is at least suitable for performing long-term measurements of NO_2 for indicative purposes, and possibly even for fixed measurements". Recent review of biases associated with Palmes tube type passive samplers by Heal et al. [67] suggests that "The effect of net bias can be reduced by application of a local "bias adjustment" factor derived from colocations of PDTs with a chemiluminescence analyzer. When this is carried out, the PDT is suitable as an indicative measure of NO_2 for air quality assessments".

To evaluate the bias, the data from passive samplers were compared to the data from selected relevant stations of the national air quality monitoring network, listed in Table 2. The national network uses chemiluminescence analyzers capable of measuring both NO and total NO_x, with NO_2 calculated as the difference of total NO_x and NO. The uncertainty of the measurements is periodically determined through analysis of reference samples, repeated measurements of the same sample, interlaboratory exercises, and for 2019, was reported to be a combination of absolute uncertainty of 2.3 μg/m^3 and a relative uncertainty of 12.3% [68].

The results of this comparison are given in Figure 2. In each case, the value reported by the passive sampler was compared to the average of hourly values from the monitoring station over the period during which the sampler was exposed. The three larger points (in red/orange) represent two samplers colocated with the Karlín monitoring station over two separate one-month periods and one sampler colocated with the Vysočanská monitoring station, show a linear correlation with a slope of 1.185 (at zero intercept; standard error of slope 0.008; differences passive sampler vs. monitoring station of +20%, +17% and +18%). While it can be argued that a regression of three points has a limited meaning, in this case, it shows that three different samplers, each used in a different time period, has produced readings that are a consistent multiple of the monitoring station data. Additionally, two samplers placed at the city urban background reference station for particulate matter (Suchdol campus of the Czech Academy of Sciences, last two lines in Table 1) during the same time period show a relative difference of 6%. These findings are in line with the 5% precision of the Palmes tube samples reported in [66].

Table 2. Measured NO_2 concentrations and average daily vehicle counts—monitoring network.

NO_2 Measurements by the National Air Quality Monitoring Network	Average of 1-h Concentrations [μg/m^3]					Average Concentrations			Traffic Vehicles/Day			Hill Climb	Inter-Section	>6 tons Excl. Zone
Station	9 March–6 April	19 March–21 April	30 August–29 September	7 September–30 October	29 September–30 October	Spring	Fall	2016–2019	Actual		Adjusted			
Legerova	46	62	45		45	54	45	51	46,300	1300	185,200		100%	1
Namesti Republiky	29	35	26		36	32	31	30	10,400	300	41,600		100%	1
Kobylisy	20	21			26	20	26	20	0	0	0			
Průmyslová	31	32			30	32	30	31	35,000	2000	35,000			
Vysočanská	29	37		31		33	31	35	37,035	3500	37,035			
Karlín		32		26		32	26	29	31,200	1200	31,200			

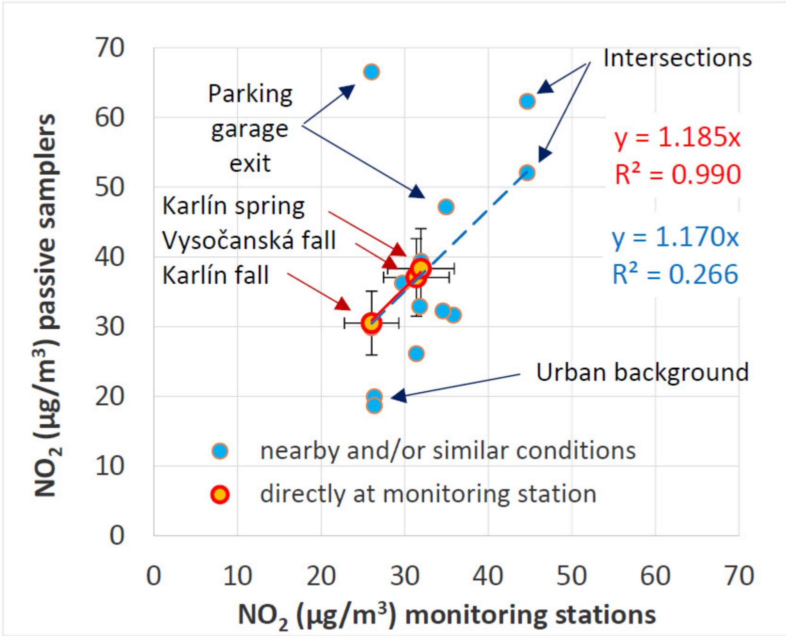

Figure 2. Comparison of passive sampler reported NO_2 concentrations to the corresponding average values from corresponding monitoring stations. Larger points circled in red denote the colocation of the sampler at the monitoring station.

Smaller blue points in Figure 2 show additional locations. Two samplers were placed at an urban background monitoring station Suchdol, however, data from this station was not available, and the readings are compared with another background monitoring station in Kobylisy. Two samplers were placed near Náměstí Republiky monitoring station, but a few dozen meters away and near an exit/entrance ramp to a large shopping center underground parking garage. Two samplers were placed on the corner of Legerova and Rumunská, near the monitoring station but at an intersection controlled by a traffic light. The readings from these four samplers were higher than from the monitoring station, which can be reasonably expected as they were near stopped and accelerating vehicles. The slope for the additional samplers was 1.17 with a standard error of 0.09; it should be noted that differences between actual NO_2 concentrations at the sampler and at the monitoring station are most likely the largest source of uncertainty.

Additional samplers close to the Legerova station (about 150 m from a large intersection) were closer to intersections and therefore exposed to additional cross-traffic, in addition to the increase in emissions rates in the vicinity of intersections. Two samplers were also placed at the Legerova monitoring station (urban hotspot) in the spring of 2019, but both were stolen. Additional samplers were placed near the Karlín monitoring station and near the Náměstí Republiky monitoring stations, and in the general vicinity of the Legerova station. The NO_2 concentrations reported for the samplers were compared with the average NO_2 concentrations measured by the monitoring station, obtained by averaging data over the time the samplers were exposed on the site.

Additional samplers used in the comparison were at reasonably close locations with not overly dissimilar traffic, and were not too far from the 15% tolerance reported by the Defra report [64]. It should be noted that the tolerance is applicable to the deviation of the sampler-reported and reference value, and not to the differences due to the samplers being at different locations with different emissions characteristics.

For all subsequent data analysis, the concentrations from the passive samplers were divided by the regression slope of 1.185. It should be noted that while this correction represents the best judgment by the authors, it is based on limited data and could be viewed as arbitrary, as the difference could arise out of the 12.3% uncertainty of the reference measurement the manufacturer-reported 18% expanded uncertainty of the passive sampler.

4.2. Comparison of NO_2 during Passive Samplers Deployment with Long-Term Averages

The variation of climatic and weather conditions is an additional source of bias to consider when comparing passive samplers to annual mean values. Figure 3 shows that the average values of NO_2 recorded at the monitoring stations over sampling periods of individual samplers (different four-week periods in March–April 2019) did not dramatically differ from annual means during the last four years (2016–2019), although differences in trends were observed among the stations. For example, the Legerova urban hotspot station exhibited an annual average of 51 µg/m^3 (2016–2019), compared to 46 µg/m^3 during the period of 9 March–April 6 and 62 µg/m^3 during 19 March–24 April. The Náměstí Republiky urban background station had a 2016–2019 average of 30 µg/m^3, compared to 29 µg/m^3 during 9 March–6 April and 35 µg/m^3 during 19 March–24 April. It should be noted that the NO_2 concentrations were generally lower during mid-March and higher during mid-April. Overall, the NO_2 concentrations during the sampling periods are believed to be representative of the annual average concentrations.

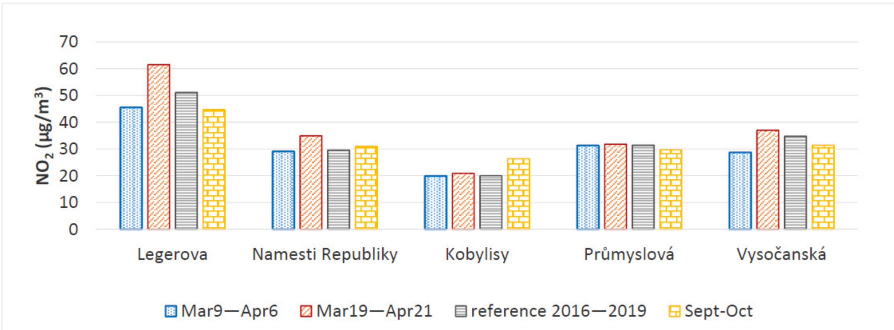

Figure 3. Comparison of monitoring station NO_2 averages during sampling periods with four-year average.

The consistency of the measurement by passive samplers during spring and fall periods is shown, along with data from the reference monitoring stations, in Figure 4. The slope of regression (with intercept forced through zero) was 0.91 ± 0.05 for the monitoring stations and 0.92 ± 0.02 for the passive samplers, showing that the monitoring stations and the passive samplers reported the same overall trends in NO_2 concentrations.

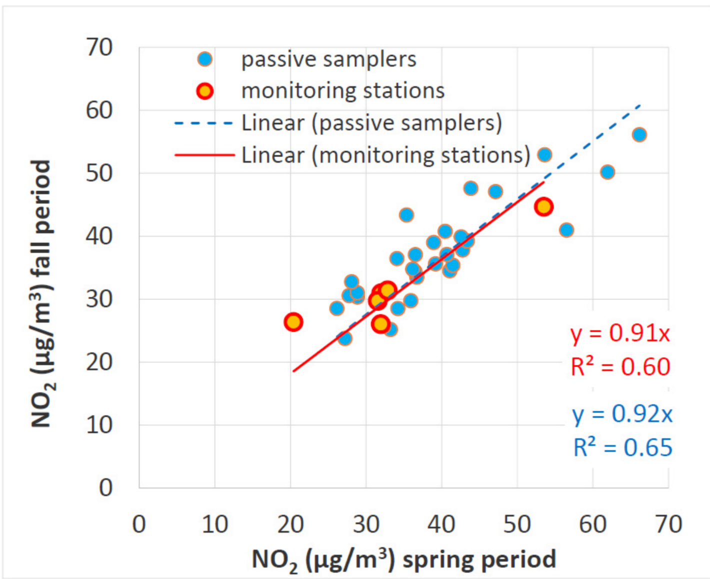

Figure 4. Comparison of spring and fall NO_2 concentrations.

4.3. Effects of Traffic

For further analysis, all passive sampler measurements were divided by a factor of 1.185 (the slope of regression of passive sampler vs. reference NO_2, see Figure 1).

The relationship between the vehicular traffic intensity and the NO_2 concentrations measured by the passive samplers is given in Figure 5. As samplers were used over two different periods, they are plotted separately in two series, one for each period, along with the average values from Legerova and Náměstí Republiky monitoring stations. It appears that there is a moderate positive trend of NO_2 increasing with traffic. Additionally, samplers located next to an uphill section of a divided highway (or a one-way street with the traffic going in the uphill direction) and next to an intersection tend to exhibit higher NO_2 concentrations. It also appears that the NO_2 concentrations are higher in urban canyons and congested streets of the city center and near intersections.

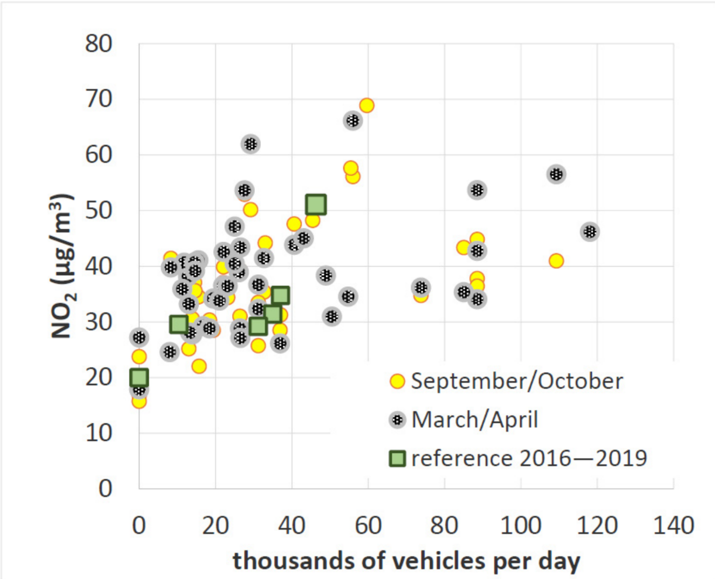

Figure 5. Relationship between traffic intensity and NO_2 concentrations measured by passive samplers in spring and fall of 2019 and by the national monitoring network (average of 2016–2019).

To assess whether high NO_2 are associated with truck traffic, samplers located in the area with limited access of vehicles over 6 tons gross weight (entry by permit only, restricted to local traffic) are plotted separately in Figure 6 (for locations where multiple samplers were used, average values are plotted). It is clear from the figure that the highest NO_2 were measured in areas where trucks over 6 tons are mostly excluded.

To account for additional emissions due to hills and intersections, the intensity of traffic traveling uphill was increased by 100% to account for additional fuel consumption, and for samplers located at intersections, the intensity of traffic was increased by 300% to account for fuel consumed at idle and when accelerating (where the intersection was without a major delay, such as time-synchronized signals at intersections of a larger one-way street with a side street or pedestrian crossing, the factor was reduced by one half). These adjustments factors were arbitrarily selected based on experience with vehicle emissions behavior (additional emissions due to climbing a hill, additional emissions due to idling at intersections and acceleration from intersections) and were independent of each other. (Note: as an example of rough calculation for a passenger car diesel engine, the acceleration of a 1500 kg car from 0 to 50 km/h requires a gain of kinetic energy of 145 kJ or 40 Wh, corresponding, at 250 g/kWh engine fuel consumption, to 10 g of fuel. The fuel consumption at idle is about 5 g/min. A one-minute stop and acceleration consumes 15 g of fuel. Driving at steady speed requires about 30 g of fuel per km, or 3 g per 100 m. If half of the cars stop and wait, the emissions in a 100 m segment around the intersection are 9 g, compared to 3 g in the case of free-flowing traffic. For simplicity, NO_x emissions are assumed to be proportional to the fuel consumption.) The relationship between the adjusted vehicle volume and NO_2 concentrations is plotted in Figure 7.

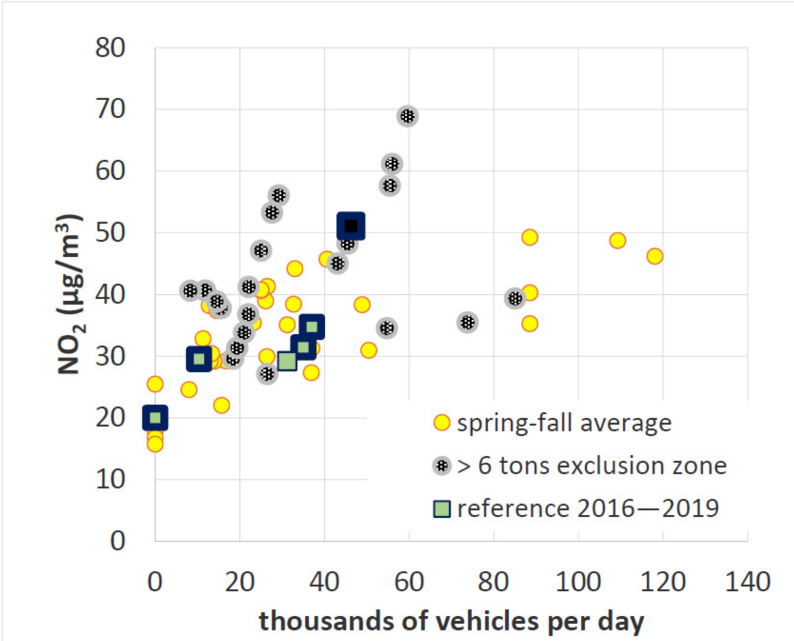

Figure 6. Relationship between traffic intensity and NO_2 concentrations measured by passive samplers (average of all measurement periods) and by the national monitoring network (average of 2016–2019).

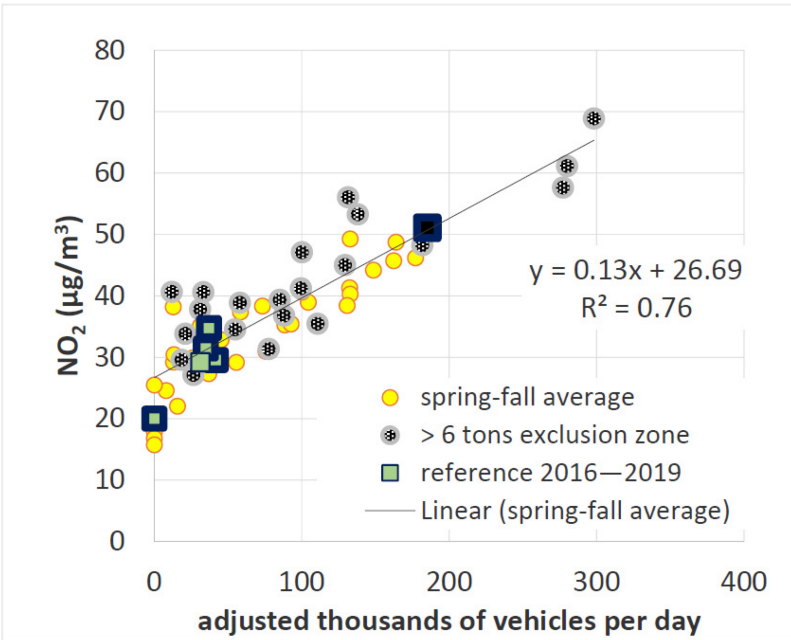

Figure 7. Relationship between adjusted traffic intensity (traffic count × (1 + fraction of vehicles travelling uphill + 3 × fraction of vehicles stopping at an intersection)) and NO_2 concentrations measured by passive samplers (average of all measurement periods) and by the national monitoring network (average of 2016–2019).

The relatively strong correlation between the adjusted traffic volumes and NO_2 concentrations (R_2 = 0.78 for September-October data and 0.76 for spring-fall averages; slope 0.13 ± 0.01; intercept 27 ± 1 μg/m^3) suggests that "local" NO_2, comprising of primary NO_2 emitted from the tailpipe and NO_2 formed locally from NO by reaction with ozone (i.e., [69]), is a considerable and in many locations dominant source of NO_2. There is no observable difference between the sampling locations where truck traffic over 6 tons was excluded and the locations where it was not excluded. Overall, there seems to be a very strong correlation between the estimated relative intensity of mobile source emissions and the measured NO_2 concentrations. It is likely that the correlation could be further improved by taking into the account distance from the traffic, traffic on adjacent streets, tunnel exits and other compounding factors.

A similar plot of the regression of the dependency of NO_2 on adjusted traffic volumes is plotted separately for the spring and fall campaigns in Figure 8, with red line denoting the legal annual NO_2 limit of 40 μg/m^3 and green line the Swiss federal limit of 30 μg/m^3 (shown for illustration in support of the health review). The regression shows that NO_2 concentrations, in all cases, increased by 0.13 μg/m^3 per 1000 vehicles daily traffic volume, adjusted for uphill and intersections, where adjusted traffic count is traffic count multiplied by a factor of (1 + fraction of vehicles travelling uphill + 3 × fraction of vehicles stopping at an intersection). It should be noted that the intercept of the regression (25–28 μg/m^3 in Figures 7 and 8; (standard error of slope is 0.01; standard error of intercept is 1 μg/m^3) is higher than the "urban background" concentrations of 15–20 μg/m^3, most likely due to accounting only for traffic on major roads and not for parking garages, taxi waiting areas, and similar locations. Even the urban background concentrations cannot be considered as NO_2 concentrations that would be theoretically be expected if no motor vehicles were operated in Prague, due to the dispersion and transport of the pollutants.

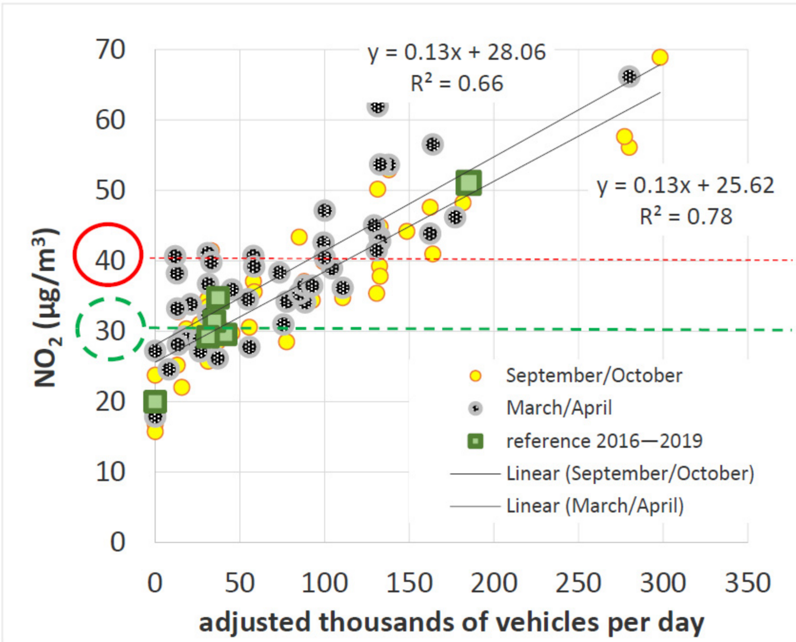

Figure 8. Relationship between adjusted traffic intensity (traffic count × (1 + fraction of vehicles travelling uphill + 3 × fraction of vehicles stopping at an intersection)) and NO_2 concentrations measured by passive samplers (average of all measurement periods) and by the national monitoring network (average of 2016–2019). EU annual limit of 40 μg/m^3 NO_2 shown as a red line, Swiss federal limit of 30 μg/m^3 NO_2 shown as a dotted green line.

Even at a rather conservative adjustment of the passive sampler readings (according to the regression, the sampler readings were 18% higher, however, this was, to a large extent, due to many samplers being at locations where the concentrations would reasonably be expected to be higher than at the corresponding monitoring station), it is clear from Figure 7 that the annual average limit of 40 μg/m^3 NO_2 is likely to be exceeded at numerous locations throughout Prague, generally, where the adjusted traffic volumes exceed the equivalent of 100 thousands of vehicles per day. This is, for example, the north-south passageway through the center city (Wilsonova, Sokolská and Legerova street) with many intersections, but also roads like V Holešovičkách (a six-lane road with 85–90 thousand vehicles per day, with a gradient of approximately 3%), a possible new hot-spot in Prague. In the worst case (intersection of two one-way streets with all vehicles traveling uphill), this limit could be reached already at 20 thousand vehicles per day, as also apparent from Figure 6.

5. Effects of Travel Restrictions on Ambient NO and NO_2 Concentrations

In order to assess the contribution of light and heavy vehicles to NO and NO_2 concentrations, hour-by-hour NO and NO_2 ambient air quality data from the national air quality monitoring network was analyzed for a period of 14 March–30 April 2020, during which travel restrictions were imposed, including the prohibition of all non-cargo international travel (truck traffic was exempted). For reference, the same period was assessed for four previous years.

A total of five stations in Prague were selected:

a. Legerova street, considered an urban hotspot, with about 45 thousand vehicles traveling daily in one direction (with similar traffic volumes in the opposite direction on a parallel street), primarily (97–98%) light-duty vehicles (trucks over 12 tons are restricted from entering inner Prague and trucks over 6 tons are restricted in the Prague historical district);
b. Vysočanská street and Průmyslová street, two traffic stations located on heavily traveled main roads used by local and transit truck traffic;
c. Náměstí Republiky, urban background station in a historical city center, on the border of pedestrian area
d. Kobylisy, a station in a suburban residential neighborhood
e. For comparison, a rural background station in Košetice, serving as the Czech national reference station, was used as a reference.

Arithmetic and geometric means and the NO_2/NO_x ratios are plotted, for each station and all years, in Table 3. A single-factor analysis of variance (ANOVA) was performed to compare the variances among the five data sets (one for the year 2020, four for each of the reference years 2016–2019) with the differences within the sets. The associated p-value (p1) was compared to the p-value (p2) associated with the difference between mean for the year 2020 and the grand mean for all five years. The higher of the p2/p1 ratio and the p2 (ensuring that the significance of the difference of the year 2020 is much higher than the difference among the years) is then considered the resulting p-value of the test.

As an alternative analysis, the statistical difference of data from each year from the combined data set for all five years was evaluated using a t-test, and the p-value associated with the test for the year 2020 was divided by the average of the four p-values associated with each of the four reference years.

It is apparent from the Table 2 that NO concentrations significantly decreased at all three traffic stations, with a highest mean decrease of 46% at Legerova and at the Košetice rural background station. The decrease in NO_2 concentrations was lower than for NO at all Prague stations, highest at Legerova (20%), and even higher (40%) at the Košetice rural background station. As vehicles emit primarily NO, the NO_2/NO_x ratio tends to increase with the age of the emissions, being lowest (around 60%) at Legerova street, 65–70% at Vysočanská, Průmyslová and Náměstí Republiky, 80% at the Kobylisy residential background station and around 90% at the rural station in Košetice. One possible interpretation of the increase in the NO_2/NO_x ratio at Legerova could be that the primary emissions of both NO and NO_2 were reduced, with lower reduction in "background" NO_2 originating from NO_x emitted elsewhere. Another possible explanation is the reaction of NO with ozone, yielding NO_2 [70]. Both March and April of 2020 were substantially sunnier than average—4 sunny days and 180 h of sunshine in March and 13 sunny days and 290 h of sunshine in April, compared to 1981–2010 average of about 3 sunny days and 120 h of sunshine for March and 3–4 sunny days and 180 h of sunshine for April [71].

Table 3. Comparison of NO and NO_2 concentrations at six monitoring stations during March–April 2020 travel restrictions with the same period during the prior four years.

	14 March–30 April	**μg/m³, Arithmetic Mean**			**μg/m³, Geometric Mean**			**Ratio**
Station	**Year**	**NO**	**NO_2**	**NO_x**	**NO**	**NO_2**	**NO_x**	**NO_2/NO_x**
Legerova	2016	43.5 ± 47.2	55.2 ± 27.4	122.0 ± 95.1	24.8 ± 3.1	48.4 ± 1.7	91.7 ± 2.2	55% ± 16%
	2017	35.4 ± 38.6	46.5 ± 28.3	100.8 ± 84.7	17.1 ± 4.0	36.8 ± 2.1	67.4 ± 2.7	57% ± 16%
type: traffic	2018	44.7 ± 46.2	59.3 ± 29.0	128.0 ± 94.3	24.6 ± 3.4	51.4 ± 1.8	95.5 ± 2.3	57% ± 17%
predominantly	2019	36.9 ± 38.2	55.0 ± 27.2	111.7 ± 81.2	21.6 ± 3.1	46.8 ± 1.9	83.9 ± 2.3	58% ± 14%
light-duty < 3.5 tons	2020	21.6 ± 27.7	43.2 ± 21.0	76.5 ± 59.3	12.2 ± 2.9	38.4 ± 1.6	60.5 ± 2.0	66% ± 15%
	2020 vs. 2016–2019	***−46% *******	***−20% *******	***−34% *******	***−44% *******	***−16% *******	***−28% *******	***+23% *******
Průmyslová	2016	24.8 ± 40.1	34.6 ± 19.8	72.8 ± 77.2	9.1 ± 4.8	29.3 ± 1.8	48.7 ± 2.4	64% ± 20%
	2017	21.9 ± 33.2	33.4 ± 20.2	67.0 ± 67.9	8.1 ± 4.8	27.3 ± 1.9	44.3 ± 2.5	65% ± 19%
type: traffic	2018	21.4 ± 35.8	31.8 ± 22.0	64.7 ± 72.4	6.5 ± 5.5	24.1 ± 2.2	38.1 ± 2.9	67% ± 20%
all types, truck transit	2019	19.7 ± 39.0	30.6 ± 21.3	60.8 ± 77.3	5.8 ± 5.2	24.3 ± 2.0	37.1 ± 2.6	69% ± 19%
	2020	16.0 ± 29.0	27.5 ± 19.4	52.0 ± 60.1	5.5 ± 4.3	21.0 ± 2.2	31.8 ± 2.7	69% ± 17%
	2020 vs. 2016–2019	***−27% *****	***−15% ****	***−22% ******	***−24% *******	***−20% *******	***−24% *******	***6%***
Vysočanská	2016	22.7 ± 29.5	38.0 ± 18.9	72.9 ± 60.4	12.0 ± 3.3	33.5 ± 1.7	55.7 ± 2.1	63% ± 16%
	2017	18.4 ± 26.6	35.1 ± 19.1	63.5 ± 56.5	8.2 ± 3.9	30.3 ± 1.7	46.6 ± 2.2	68% ± 17%
type: traffic	2018	18.8 ± 25.1	36.0 ± 19.9	64.9 ± 54.7	7.8 ± 4.3	30.5 ± 1.8	46.9 ± 2.3	68% ± 18%
all types, truck transit	2019	17.4 ± 22.3	34.1 ± 19.1	60.8 ± 49.9	8.7 ± 3.5	28.9 ± 1.8	45.5 ± 2.2	66% ± 16%
	2020	14.2 ± 19.9	33.2 ± 18.9	55.1 ± 45.0	7.0 ± 3.3	28.1 ± 1.8	41.8 ± 2.1	70% ± 16%
	2020 vs. 2016–2019	***−27% ******	***−7% *******	***−16% *******	***−23% *******	***−9% *******	***−14% *******	***8%***
Náměstí Republiky	2016	12.0 ± 14.0	20.2 ± 7.1	38.8 ± 26.4	6.9 ± 3.2	19.2 ± 1.4	33.3 ± 1.7	59% ± 26%
	2017	12.1 ± 12.5	33.1 ± 14.6	51.7 ± 30.8	9.4 ± 1.9	30.4 ± 1.5	46.0 ± 1.6	66% ± 15%
	2018	15.6 ± 19.5	35.2 ± 17.7	59.1 ± 43.7	9.8 ± 2.6	31.5 ± 1.6	49.1 ± 1.8	65% ± 18%
type: urban	2019	10.9 ± 14.2	31.9 ± 15.2	48.7 ± 33.5	7.5 ± 2.1	28.9 ± 1.5	41.9 ± 1.7	70% ± 13%
background	2020	10.8 ± 10.6	27.8 ± 14.5	44.6 ± 28.2	8.0 ± 2.1	24.9 ± 1.6	38.4 ± 1.7	66% ± 12%
	2020 vs. 2016–2019	***−14%***	***−7%***	***−10%***	***−3%***	***−8%***	***−9%***	***2%***
Kobylisy	2016	3.8 ± 9.3	10.4 ± 6.3	16.3 ± 19.0	1.2 ± 3.4	9.1 ± 1.7	11.9 ± 2.0	80% ± 16%
	2017	3.7 ± 9.4	14.5 ± 8.7	19.7 ± 19.9	1.5 ± 3.1	12.7 ± 1.7	15.4 ± 1.9	80% ± 16%
type: residential	2018	3.7 ± 8.8	21.7 ± 15.9	27.5 ± 26.0	1.4 ± 3.2	17.2 ± 1.9	20.4 ± 2.1	86% ± 11%
background	2019	3.4 ± 8.8	19.6 ± 15.7	25.0 ± 27.1	1.1 ± 3.2	15.8 ± 1.9	18.4 ± 2.0	87% ± 14%
	2020	2.8 ± 5.9	17.3 ± 14.1	21.0 ± 20.8	1.5 ± 2.3	13.0 ± 2.1	14.8 ± 2.2	81% ± 14%
	2020 vs. 2016–2019	***−22%***	***4%***	***−5%***	***14%***	***−2%***	***−8%***	***−6%***
Košetice	2016	0.5 ± 0.6	6.0 ± 2.6	6.8 ± 3.1	0.3 ± 2.0	5.4 ± 1.6	6.2 ± 1.6	90% ± 7%
	2017	0.3 ± 0.4	7.3 ± 3.0	7.8 ± 3.2	0.3 ± 1.8	6.7 ± 1.5	7.2 ± 1.5	93% ± 5%
national reference	2018	0.3 ± 0.4	3.9 ± 2.7	4.3 ± 3.0	0.2 ± 2.6	3.1 ± 2.0	3.5 ± 1.9	90% ± 9%
background	2019	0.2 ± 0.3	3.6 ± 1.9	4.0 ± 2.1	0.1 ± 2.9	3.1 ± 1.8	3.5 ± 1.7	91% ± 9%
outside of Prague	2020	0.2 ± 0.3	3.1 ± 1.7	3.5 ± 1.9	0.1 ± 2.8	2.7 ± 1.8	3.0 ± 1.8	90% ± 9%
	2020 vs. 2016–2019	***−27% ******	***−7% *****	***−16% ******	***−23% *****	***−9%***	***−14% ****	***+8% ******

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$.

It should be noted, however, that the interplay of different factors is rather complex. For example, diminished traffic volumes result in lower frequency of low-speed driving in congested areas, during which the efficiency of exhaust aftertreatment is reduced, resulting in higher overall exhaust temperatures (and thus higher production of NO_2 in oxidation catalysts), but also higher probability of SCR functionality (and thus lower NO_x emissions)—however, due to Dieselgate, the reality of NO_x aftertreatment efficiency is likely to be variable, questionable and poorly known.

Additionally, according to [72], it appears that on-road oxidation of NO by ambient O_3 is a significant, but so far ignored, contributor to curbside and near-road NO_2. This is in agreement with on-road NO_2/NO_x ratios in U.S. being reported to be 25–35% and substantially higher than anticipated tailpipe emissions rates [73].

6. Discussion

A detailed analysis of NO_2 concentrations measured by the passive samplers shows a clear correlation of NO_2 concentrations with daily traffic counts, adjusted for additional emissions due to uphill travel and stopping at intersections. This finding is in good agreement with the data from the monitoring stations, which, by themselves, are too sparse to make such inference. The correlation of NO_2 concentrations with vehicular traffic intensity is also apparent from the comparison of the data from state air quality monitoring stations during the period of 14 March–30 April 2020, during which travel restrictions were imposed, including the prohibition of all non-cargo international travel, with comparable periods of four previous years. Overall, the findings confirm that vehicular traffic, through primary NO_2 emissions (and possibly through fast reaction of primary NO with ozone), directly affects the NO_2 concentrations in the immediate vicinity.

This correlation, along with correlation of passive sampler readings and air quality monitoring stations, and good consistency of reported NO_2 concentrations among samplers used within the same location at different time periods, all suggest that passive samplers appear to provide, at a reasonable cost and effort, a fairly good image of the distribution of NO_2 concentrations. Judging from limited data, the passive samplers were found to measure about 18.5% higher values than the monitoring stations. Repeated—and most likely deliberate—removals of passive samplers from the immediate vicinity of the monitoring stations have prevented a more quantitative comparison. A comparison of a broader set of data reveals a slightly smaller bias, contributed to, in several cases, by the passive samplers being at more exposed locations (i.e., near the exit of a large underground parking garage) than the monitoring stations. The true bias could therefore be possibly even lower.

Since the trends are comparable within and outside the heavy truck exclusion area, this seems to be primarily an effect of cars and other lighter vehicles (per city statistics, about 90% of traffic is passenger cars [63]). Additionally, there is no correlation between the measured NO_2 concentrations and the heavy vehicle traffic count or between the measured NO_2 concentration and the fraction of heavy vehicles. This is in line with the findings that truck NOx emissions have decreased to a considerably higher extent than those of diesel cars in Europe.

The samplers at the locations with highest fraction of heavy vehicles (10–15%, vs. average for all locations 4%) and with the highest absolute heavy vehicle counts (7–16 thousands/day, vs. average 1.7 thousands/day) have measured 25–35 $\mu g/m^3$ NO_2, which is in the second lowest quartile (median concentration is 35 $\mu g/m^3$). This may also be, in part, due to a dependent factor that heavy vehicle traffic is limited in the high population density city center.

The monitoring station at Legerova street is most likely not the absolute hot-spot—it is expected that the emissions of NO_x would be higher on the parallel street where the vehicles travel uphill (Legerova is one-way street downhill) and at nearby intersections. The street V Holešovičkách, a six-lane road, which is, unlike most other roads of similar size, immediately bordered by residential neighborhoods, with a traffic intensity approaching 100 thousand vehicles per day, a major increase after the opening of a new complex of tunnels providing an alternative route through congested areas, further complicated by a 3% grade, could easily be the next traffic hot-spot.

Considering the finding that about half of the vehicles traveling on the road are not older than 7 years [27], and the several-fold decrease in NO_x emissions standards over the last decade and half, a much sharper decrease of NO_2 concentrations would be expected than the approximately 1% annually reported by Hůnová [5]; a higher reduction of about 2.5% annually was observed in Western Europe, and about 4.7% annually in United States and Canada [74]. Given the decrease in the limit values of roughly two thirds from Euro 3 (0.50 g/km NO_x, 2000) to Euro 5 (0.18 g/km, 2009–2010) and from Euro 4 (0.25 g/km NO_x, 2005) to Euro 6 (0.08 g/km, 2014–2015), the introduction of Euro 5 in late 2009 and Euro 6 in late 2014 should have resulted in about a two thirds NO_x reduction in at least half of the vehicles, or about one third reduction in NO_x emissions in general. As learned from the analysis of the effects of traffic restrictions, the effect on NO_2 concentrations may be different, and possibly somewhat smaller than the reduction in NO_x emissions, due to atmospheric chemistry. The effects of such a decrease could also have been diminished by an increase in traffic, however, in the center city, the intensity of automobile traffic has been stagnating, or even slightly decreasing.

The mediocre decrease in NO_2 concentrations, despite more dramatic reduction being expected from improving vehicle technology, is in line with earlier findings that the real NO_x emissions of diesel vehicles did not decrease despite the decreasing emissions limits. The situation should have been, however, substantially remedied by "post-Dieselgate" vehicles and by repairs of vehicles affected by Dieselgate. Since it was not, a question therefore arises as to the possibility that Dieselgate relevant repairs were not done on a sufficient number of vehicles and/or were not sufficiently effective and/or were reversed to the "original factory conditions" by the vehicle owners. The authors do not have any reliable statistics on this matter. Furthermore, considering that all three mentioned situations could be associated with criminal offenses and/or considerable civil penalties, detailed investigation of the matter is likely to be considerably difficult.

If there is no assurance that the NO_2 concentrations will decrease dramatically due to a radical improvement in primary NO_x emissions, the only other suitable strategy to improve the air quality is to reduce, to the extent required, the intensity of vehicular traffic. Contrary to the remote regions where automobiles are, in most cases, the only practical means of travel, Prague has an extensive network of public transit. According to the City of Prague statistics [63], only 29% of trips in Prague are done by automobile, 26% of trips are by walking and 42% of trips by public transit. Of the public transit, slightly over one third is done by subway, and another third by trams and commuter rail, which are, with the exception of a rather small number of diesel rail cars used on sparsely traveled rail lines, run on electric power, and therefore with very small effect on NO_2 emissions. The remaining third of trips is by diesel buses, the majority of which are equipped with SCR catalysts, and potentially reaching NO_x emissions not much larger (and according to measurements possibly even smaller) levels, per kilometer and vehicle, than an average diesel car. It is therefore readily apparent that shifting from an average automobile to any other means of transport is likely to reduce the NO_2 concentrations. (Shift to electric power, compressed natural gas, or other "clean" propulsion is a gradual process and is unlikely to be done, within a few years, on a sufficiently large number of vehicles to make a difference throughout the city).

7. Summary and Conclusions

Despite massive reductions in diesel cars NO_x emission limits, of about two thirds from Euro 3 to Euro 5 and from Euro 4 to Euro 6, NO_2 concentrations throughout the Czech Republic have been decreasing at a mediocre rate of 1% annually.

A review of the underlying engine emissions trends shows that the conversion of NO into NO_2 in diesel oxidation catalysts, beneficial for regeneration of diesel particle filters and for the functioning of the SCR systems for NO_x reduction, did not, contrary to the intentions of the legislation, go hand in hand with a major reduction of NO_x emissions in subsequent (downstream) NO_x aftertreatment devices. As a result, primary NO_2 emissions from light duty diesel vehicles are in most cases considerably higher than intended in the emissions legislation due to non-adherence of many manufacturers to the primary intent of the legislation.

A review of the health effects on NO_2 on children shows that all reviewed studies indicate a significant effect of prenatal NO_2 exposure to children´s neurobehavioral development, in adults to dementia at concentrations lower than EU standards of 40 $\mu g/m^3$/year. These results should be understood as a strong recommendation to reduce the NO_2 concentrations below the current EU standard. All presented studies prove that NO_2 can significantly deteriorate CNS and therefore this knowledge should be used to improve the quality of our lives.

To elucidate the effects of motorized traffic on NO_2 concentrations, data from 104 passive NO_2 samplers deployed at 65 locations in Prague during March–April and September–October of 2019 were examined. Comparisons with the national monitoring network show a positive bias of 18.5% for colocated samplers and 17% for samplers nearby (or in similar settings as) the monitoring stations. There was a good correlation among repeated measurements at the same locations. The data from the national air quality monitoring network show that the average concentrations in both spring and fall sampling periods were consistent with 2016–2019 averages.

The average measured NO_2 concentrations at the selected locations, after correcting for the 18.5% bias, were in the range of 16–69 $\mu g/m^3$, with a mean of 36 $\mu g/m^3$ and a median of 35 $\mu g/m^3$, and were higher than the EU and national limit (annual average) of 40 $\mu g/m^3$ at 32% of locations. The NO_2 concentrations have correlated well with the intensity of traffic (average daily vehicle counts), corrected for additional emissions due to uphill travel and due to idling at, and accelerating from, intersections. Several additional "hot-spots" were identified, in addition to the "hot-spot" monitoring station at Legerova street (2016–2019 NO_2 average of 51 $\mu g/m^3$), where the vehicles travel on a slight decline on a one-way street: several intersections at Sokolská street, parallel with Legerova with uphill direction of travel, and emerging hot-spots along V Holešovičkách street, where the traffic intensity increased due to the opening of a new series of tunnels. Analysis of the effect of coronavirus related travel restrictions were evaluated by comparing the data from six monitoring stations (15 March–30 April 2020, relative to the same period during 2016–2019) reveal a reduction of NO, NO_2 and NO_x (except for a small increase of NO_2 at one of the background stations), with NO reduction being, at high traffic locations, higher than that of NO_2. The spatial analysis of data from passive samplers and time analysis of data during the travel restrictions both demonstrate a consistent positive correlation between traffic intensity and NO_2 concentrations along/near the travel path.

It appears that decreases in vehicle NO_x emission limits, introduced in the last decade or two, have failed to sufficiently reduce the ambient NO_2 concentrations in exposed locations in Prague. This is in part due to increased fraction of NO_2 in NO_x in newer vehicles, and in part due to "a major disparity between the numerical value of the emission limit and the actual emissions in everyday driving". Further, there is no apparent sign of, and it is far from clear that, the "excess emissions" of NO_x, a problem known as Dieselgate, have been efficiently remedied.

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