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Effect of Vehicle Classification and Activity on Field Evaluation of Photocatalytic Concrete Pavements' Ability to Remove Nitrogen Oxides – A Case Study

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Abstract: There has been an increasing interest in photocatalytic pavements, which can decompose pollutants to nonhazardous waste products with little energy requirements and selectivity. The objective of this study is to evaluate the effects of vehicle activity and classification on nitrogen oxide (NO_x) pollution emitted and correlating these factors to the NO_x reduction from photocatalytic pavements. To achieve this objective, a field study was conducted with 22.3 m^2 of photocatalytic spray coated area and 22.3 m^2 of uncoated control area. Evidence of photocatalytic reduction of NO_x was evaluated by directly measuring NO_x reductions from the ambient air. A traffic study was conducted for the photocatalytic control areas to characterize the variability in traffic classification and activity between the two areas and its effects on interpreting NO_x reduction. Results showed that the amount of NO_x emitted in the area predicted to be from traffic sources is no more than 5 grams per hour. Due to the low values of pollution emitted in the both the photocatalytic area and the control area, minor differences in traffic activity between these two areas resulted in significant differences in the amount of pollution emitted between the photocatalytic and the control areas. This may complicate the interpretation of the NO_x reduction results. Furthermore, there was no significant linear correlation of vehicle class and speed and NO_x reduction.

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***Key words**: Nitrogen oxides; Photocatalytic pavements; Sustainable concrete pavement; Titanium dioxide.*

Introduction

Nitrogen dioxide is one of six criteria pollutants that the Environmental Protection Agency (EPA) is required to set National Ambient Air Quality Standards (NAAQS) under the Clean Air Act. Currently, over 45 million people are living within 91.5 meter of an airport, railroad, or major highway and this value is increasing [1, 2]. Yet vehicle emissions contain more NO compared to NO_2, NO is easily converted to NO_2 in a reaction with O_3, making reduction of NO equally as important. As a result, there has been an increasing interest in photocatalytic pavements, which can decompose pollutants to nonhazardous waste products with little energy requirements and selectivity [3, 4]. Laboratory results show that photocatalytic pavements may reduce pollutants such as NO_x by as much as 40% to 85% once pollutants are emitted in the air [5]. In addition, photocatalytic pavements have the advantage that they may be a cost-effective air pollution abatement technique since they may be applied only to target areas.

Understanding of photocatalytic pavements in real-world settings is essential not only to comprehend its effectiveness but also to be included into SIP air quality calculations and models in efforts to include photocatalytic pavements as a possible pollution reduction strategy. The current understanding of photocatalytic pavements in real-world settings is still lacking. Lab studies have shown photocatalytic reduction of NO_x depends on many environmental factors impacting its efficiency including, humidity, concentration, temperature, light intensity, and wind speed. A detailed analysis of how environmental parameters including solar radiation affected field conditioned was presented in previous papers [6-7]. Unfortunately, the quantification of NO_x reduction in field studies is difficult and challenging due to these environmental factors and many others that exist in real world settings. Current field studies have confirmed that relative humidity, wind speed and direction, light intensity, and solar radiation impact the NO_x reduction; however, research studies were not able to identify a clear reduction due to additional parameters such as vehicle activity and classification.

Two techniques to measure photocatalytic degradation from field studies are available. The first is to measure the reduction directly by measuring the ambient air pollution concentration and the second is to measure the reduction indirectly by measuring byproducts created from the degradation process. For nitrogen oxides, the approved method of ambient air NO_x detection is chemiluminescence, which continuously monitors NO_x concentrations. This is challenging since environmental parameters are constantly changing. Whereas the indirect technique to measure photocatalytic reductions of NO_x, is to measure NO_3 and NO_2 deposited on the pavement surface. Nitrates and Nitrites are water-soluble and therefore, they are washed from the surface with water [8]. Water samples are usually collected daily and analyzed for nitrates and nitrites, thus it does not capture the environmental variability essential for understanding photocatalytic reduction of NO_x in real world environments. Nevertheless, measuring nitrates does offer evidence of a photocatalytic reaction occurring at the surface.

To directly measure pollutants' reduction, continuous emission monitors have been used to measure the ambient NO_x

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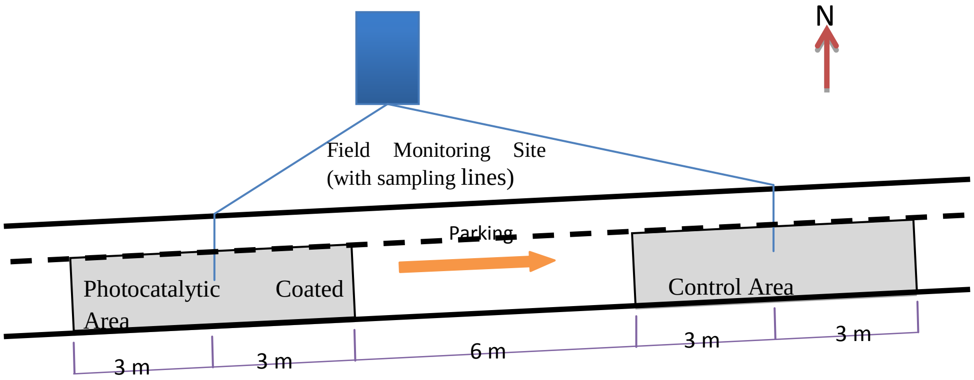

Fig. 1. Field Site Location and Ambient Air Monitoring Equipment.

concentrations. Since the results are continuous, this allows for correlation to other environmental factors that can be monitored. In order to determine the photocatalytic reduction, simultaneous measurements are preferred. Therefore, photocatalytic pavement areas NO_x concentrations and non-photocatalytic pavement areas NO_x concentrations are compared under similar environmental conditions. This technique requires significant investment in equipment to measure both sites concurrently. As a result, few field studies exist using the direct measurement. Nevertheless, Li and Qian [9] found a photocatalytic reaction occurring in the field with reductions as high as 80%; however, results were not correlated to any environmental conditions [9]. In efforts to correlate NO_x reduction effectiveness to environmental conditions, previous work by the authors recorded traffic and meteorological data as well. Results confirmed that relative humidity, wind speed and direction, light intensity, and solar radiation all impact NO_x reduction [10].

Additional factors that need to be considered include varying vehicle activity and vehicle classification [10]. Vehicle traffic emissions vary by both vehicle classification and by vehicle activity. While driving, vehicles cycle between stopping, starting, cruising, accelerating, and decelerating. During this time, the NO emitted varies depending on the drive cycle whether the vehicle is idle, accelerating, decelerating, or cruising [11]. The EPA monitors these emissions and has developed a modeling system to predict emission factors per vehicle type and activity. The motor vehicle emission simulator (MOVES) is the latest version that was released in 2010 [12]. Due to the large impact of vehicle activity and class on the concentration of NO emitted, this is a factor that must be incorporated and monitored in field studies.

Research Objectives

The objective of this study is to evaluate the impact of vehicle activity and classification on NO_x pollution emitted and correlating this variation with NO_x reduction from photocatalytic pavements. Results of this study will assist the development of upcoming photocatalytic field studies and will also allow understanding of where photocatalytic pavements may prove most useful.

Experimental Program

The field study consisted of an 18.3m concrete pavement roadway located on Raphael Semmes Road on Louisiana State University's campus. Because this is an already existing roadway, the photocatalytic coating was applied using the spray coating technique. The coated section was 3.7m wide being the width of the lane, by 6.1 m long. A control area of a similar size was separated from the photocatalytic coated area by 6.1 m; thus allowing for 9.1 m between the two sampling lines (Fig. 1). The test equipment is housed in a trailer, centrally located, such that NO_x concentrations can be simultaneously measured from both the coated and uncoated areas. To characterize environmental conditions, NO_x ambient air pollution and weather factors were collected directly from the field site. In addition, due to the variability of the traffic resulting from the parking area, a traffic study was conducted to identify vehicle speed and vehicle classification for both areas. Results from the traffic study were used to understand the difference in NO_x emitted in the photocatalytic coated area versus the control area by estimating the emission rates using MOVES. Furthermore, a correlation study was conducted to determine the significance of each parameter recorded.

Field Photocatalytic Spray Coat Application

In preparation for TiO_2 spray application, the 3.7m by 6.1m area to be coated was divided into 0.6m x 0.6m grid. Before application, the roadway was cleared of any debris by sweeping. The spray coat (PURETI®) consisted of anatase TiO_2 nanoparticles suspended in an aqueous binder at 2% by volume.

The spray coat was applied using a hand spray gun (Fig. 2) using a crosshatch formation at 96.8 ml/m^2. Therefore, 36 ml of sample was measured out for each 0.6m x 0.6m square of the grid. This equates to a 0.21 mg/cm^2 catalyst-loading rate.

Environmental Conditions Detection

Environmental conditions were recorded during the monitoring period. Weather data was collected and stored in order to interpret different trends in the measurements. The weather station employed, Davis 6152 Wireless Vantage Pro, measured and stored ambient air temperature, relative humidity, wind speed, wind direction, barometric pressure, precipitation (rainfall and rain rate), and solar radiation per minute.

Fig. 2. TiO_2 Spray Coat Application.

Traffic Study

Due to the irregularity of the traffic in the field study area, a manual traffic study was conducted during the monitoring period to detect differences in vehicle classification, activity, and counts between the photocatalytic area and the control area. The traffic data was collected for the photocatalytic coated area and the control area separately per minute to align with the NO_x concentration measurements. Since the photocatalytic pavement requires sunlight, data was collected from dawn to sunset summing to a week. A tally sheet was used to classify the vehicle type and estimate vehicle speed.

The vehicle types were classified according to the EPA Motor Vehicle Emission Simulator (MOVES) source types. Only the transit bus and short haul trucks were used since it was difficult to differentiate between the various buses source types and between short and long haul trucks defined by MOVES. Therefore, the resulting MOVES source types identified for the traffic study are shown in Table 1 with the HPMS equivalents [13-14]. Vans and SUVs were considered as part of the passenger truck source type according to the HPMS other 2 axle-4 tire vehicle definition [13]. Commercial trucks and vans were considered as part of the light commercial truck source type. The speed limit of the roadway is 16.1 km/h. Therefore, the vehicle speed was separated according to the MOVES speed bins shown in Table 2 with the addition of idling.

Moves Emission Calculations

To gain a better understanding of the NO_x emitted from the field site area, the field site weather and traffic data was used to create a project level database for MOVES to calculate the hourly emission rates [14]. The project level consisted of two links, one being an urban unrestricted road and the second being the off network portion for the parking spaces. The off network startup fraction, the number of startups per hour over the population of vehicles during the hour, were estimated by the parking meter data by assuming the end time of the parking meter was when the car started up. Since the traffic study was completed for the photocatalytic area and control area separately, the emission rates were calculated for both test areas separately. This allowed for characterization of the impact of the irregularity of the traffic over the two sections on the NO_x pollution. MOVES default settings were used for the fuel formulation, fuel supply, age-distribution and operating mode, which was calculated by the average speed methodology. The average speed was estimated as 10 mph being the speed limit.

Table 1. Vehicle Classification MOVES Correlated to HPMS.

Source Type ID	Source Types	HPMS Vehicle Type ID	HPMS Vehicle Type
11	Motorcycle	10	Motorcycles
21	Passenger Car	20	Passenger Cars
31	Passenger Truck	30	Other 2 axle-4 Tire Vehicles
32	Light Commercial Truck	30	Other 2 axle-4 Tire Vehicles
42	Transit Bus	40	Buses
52	Single Unit Short-haul Truck	50	Single Unit Trucks
61	Combination Short-haul Truck	60	Combination Trucks

Table 2. MOVES Speed Bins

Bin	Average Speed (mph)	Average Speed Range (mph)
0	0	Idling
1	2.5	Speed < 2.5 mph
2	5	2.5 mph ≦ speed < 7.5 mph
3	10	7.5 mph ≦ speed < 12.5 mph

NO_x Ambient Air Detection

NO_x concentrations were monitored for both the coated and uncoated sections, simultaneously using Thermo NO_x analyzers. The NO_x analyzers meet the USEPA requirements for RFNA-1289-074 and were calibrated in accordance to EPA standards using the gas phase titration (GPT) method [15, 16]. A zero-span check was conducted regularly for quality control as recommended by EPA to ensure proper calibration and operation of the equipment [16]. Equipment was recalibrated when the percent error was over 5%.

The sample lines were located at the pavement level centered in the photocatalytic area and control area as shown in Fig. 1 and pictured in Fig. 3. To withstand the traffic, the sample lines were made of 316 stainless steel, an approved material for NO_x sampling. NO, NO_2, and NO_x concentrations were continuously measured and were stored as minute averages. During events of heavy rain, sampling was discontinued to protect the equipment.

Correlation Analysis

The recorded NO_x reduction was correlated with environmental parameters including vehicle speed and vehicle classification using the Pearson Correlation Coefficients. The Pearson Correlation Coefficient and the associated p-value were calculated using SAS.

Fig. 3. NOx Air Sampling Line.

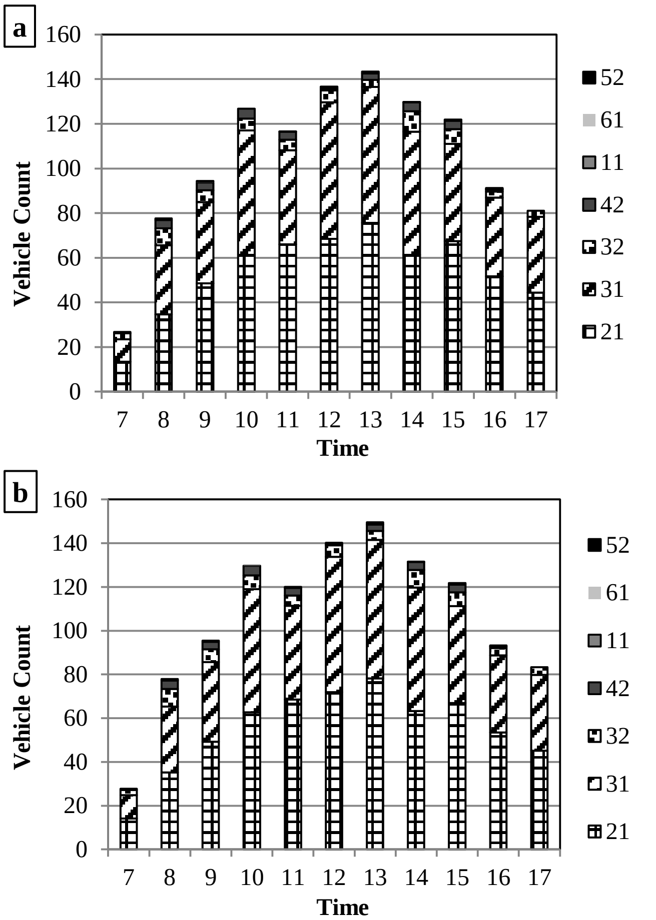

Fig. 4. Vehicle Classification per Hour as Defined in Table 1; (a) Control, (b) Photocatalytic.

Results and Analysis

Traffic Study Vehicle Class

Results from the traffic study illustrate that there is minor variation between the hourly average traffic counts over the control section and the photocatalytic section. Fig. 4 represents the total average vehicle count and distribution of the moves vehicle classes as

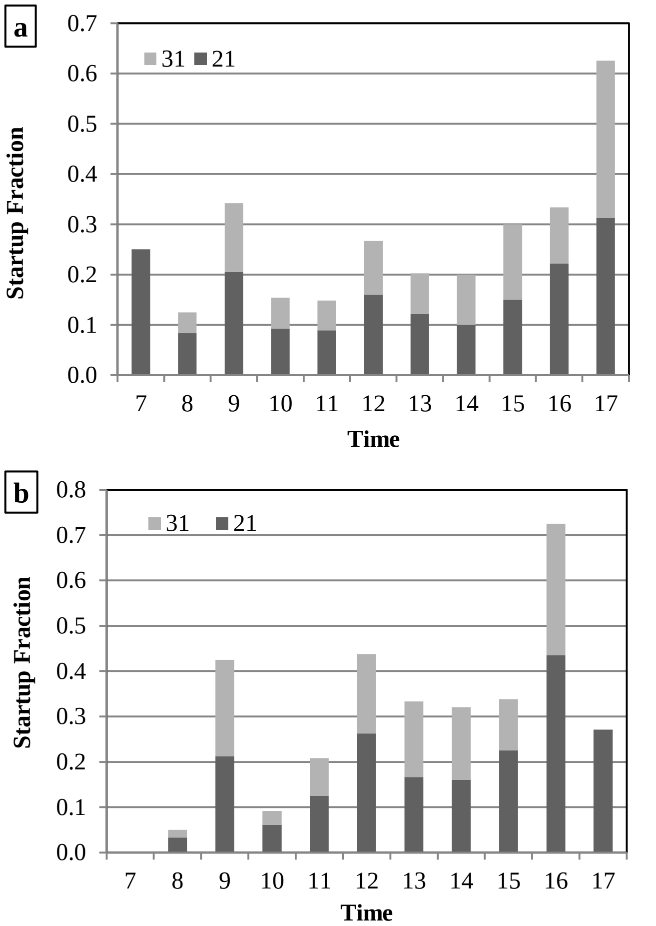

Fig. 5. Vehicle Startup Fractions per Vehicle Classification as Defined in Table 1; (a) Control, (b) Photocatalytic.

defined in Table 1 per hour determined by the traffic study for both the control and photocatalytic sections. As shown in Fig. 4, the majority of the traffic is passenger cars and trucks. The vehicle classification does not change significantly from hour to hour. The peak traffic is around 13:00 reaching 143 total vehicles for the control area and 150 total vehicles for the photocatalytic pavement area. In general, the photocatalytic coated area had a slightly higher hourly vehicle count. This is reasonable due to the vehicles parking before reaching the control area.

Fig. 5 illustrates the off network portion average startup fraction estimated from the parking meter data. As expected, photocatalytic section and the control section startup fractions are different complicating interpretation of NO photodegradation results.

To understand the significance of this variation, these results were incorporated into MOVES to characterize the difference in emissions rates. Fig. 6 illustrates NO and NO_2 emission factors predicted for the photocatalytic and control sections from MOVES. As shown in this figure, the results show that the NO_x pollution emitted from the vehicles in this area is not significant. The highest amount of NO_x emitted in either the control or the photocatalytic area due to the traffic is no more than 5 grams over an hour. However, it is clear that the photocatalytic coating area had higher predicted NO_x pollution emissions compared to the control area. The difference in NO_x concentrations emitted in the two areas could mislead results. Higher concentrations being emitted in the

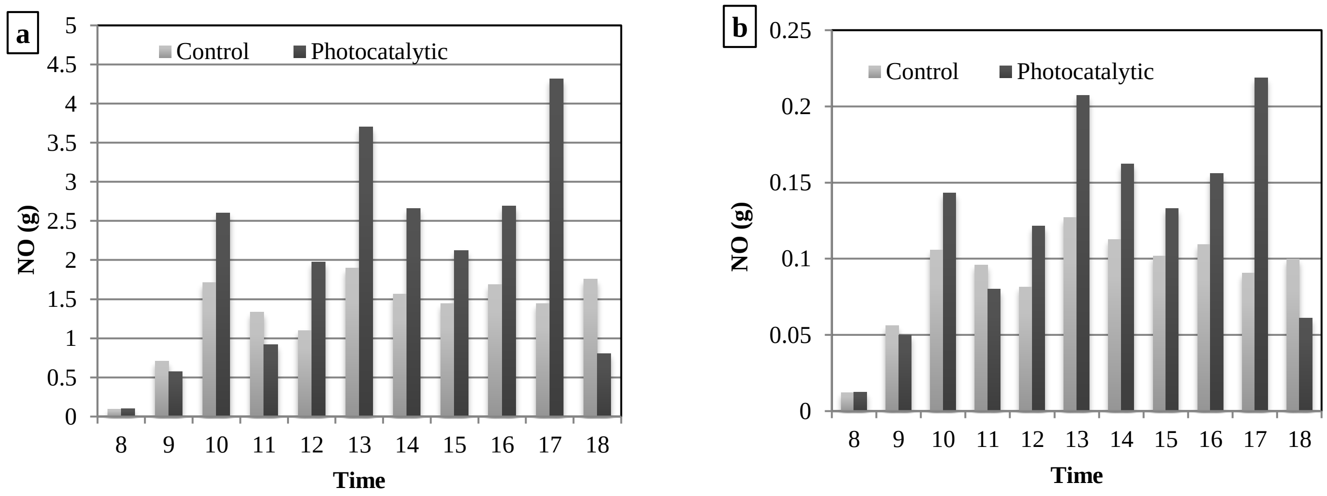

Fig. 6. MOVES Predicted Emission Factors; (a) NO, (b) NO2.

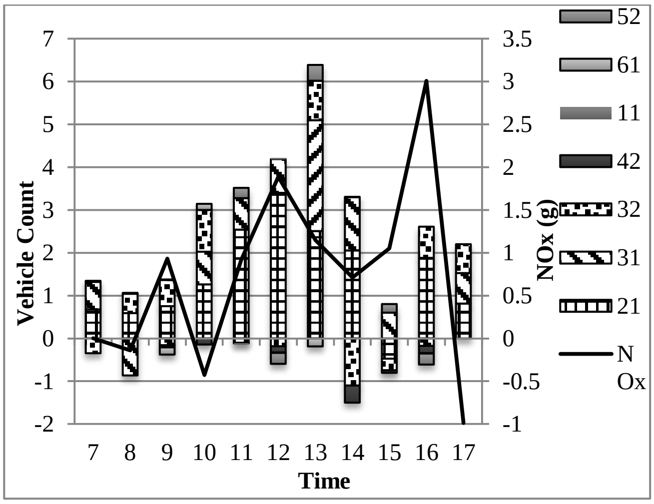

Fig. 7. Difference Vehicle Count, Classification (Table 1) and MOVES Predicted NO_x Emissions in Photocatalytic Area from Control Area.

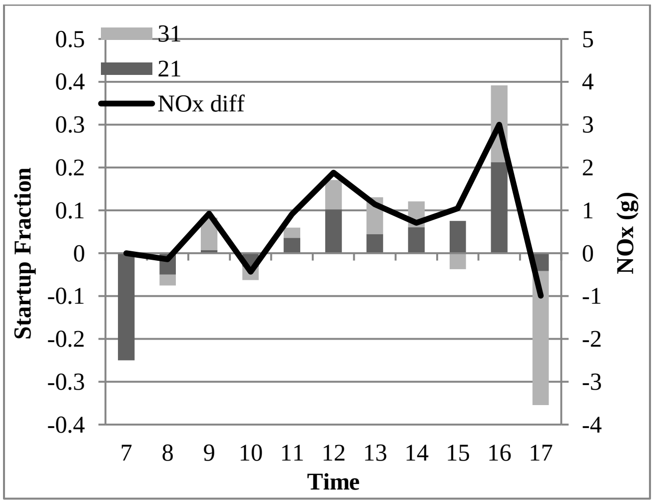

Fig. 8. Difference Startup Fractions by Vehicle Classification (Table 1) and MOVES Predicted NO_x Emissions in Photocatalytic Area from Control Area.

photocatalytic area could be offsetting or reducing any NO_x reduction calculated.

Fig. 7 compares the difference of the vehicle counts previously discussed in relation to the difference of the predicted NO_x emissions for the photocatalytic area versus the control area. From this figure, it is evident that even though there is only a slight difference in the vehicle counts, there is a signficant difference in the predicted NO_x emitted especially when compared to the low total predicted NO_x emissions. However, not all of the differences seem to be described by the vehicle counts. As a result, Fig. 8 compares the difference in startup fractions in relation to the difference of the predicted NO_x emissions for the photocatalytic area versus the control area. The startup fractions further explain the differences in hourly pollution emission rates predicted. For example at time 10 and 17, although there was more traffic on the photocatalytic area, there was more startups in the control area resulting in NO_x predicted higher emissions in the control area.

Hourly NO_x Reduction Recorded

With these results, it is not surprising that the average hourly NO_x reduction recorded in the field study is not easily comprehensible. Fig. 9 details the average NO_x reduction recorded in the field compared to the difference in the predicted NO_x emissions. As shown in this figure, there was no clear correlation between the average NO_x reduction recorded in the field and the difference in the predicted NO_x emissions. This could be possibly due in part to the NO_x reduction due to photocatalytic pavement being offset by the higher NO_x pollution.

NO_x Reduction Correlation

The Pearson's coefficient of correlation was calculated to evaluate the degree of linear association between the NO_x reduction and the difference in vehicle class and vehicle speed recorded for the photocatalytic and control area per minute. This allowed to evaluate if the difference in vehicle activity had a significant impact on the interpretation of the NO_x reduction recorded. The coefficient of correlation was calculated for the vehicle class, vehicle speed, and combination of the two parameters. The results from the

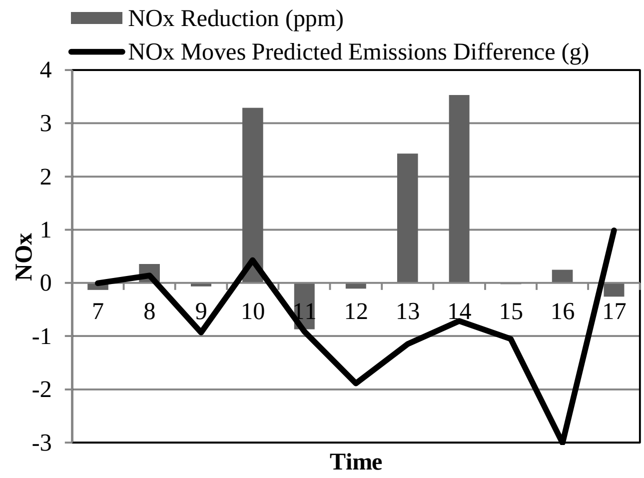

Fig. 9. NO_x Reduction Compared to MOVES Predicted Emission.

Table 3. Pearson Correlation Coefficients for Vehicle Class.

Source Type ID	Source Types	Pearson's Coefficient	P-value
11	Motorcycle	.	.
21	Passenger Car	0.0081	0.6553
31	Passenger Truck	-0.05516	0.0023
32	Light Commercial Truck	-0.00849	0.6397
42	Transit Bus	0.03379	0.0623
52	Single Unit Short-haul Truck	0.00029	0.9872
61	Combination Short-haul Truck	-0.00323	0.8586

Table 4. Pearson Correlation Coefficients for Speed Bins.

Bin	Pearson's Coefficient	P-value
0	0.02282	0.2081
1	-0.02784	0.1246
2	-0.00077	0.9660
3	-0.00828	0.6477

pairwise correlation for the vehicle class and vehicle speed are found in Tables 3 and 4, where the top number represents the coefficient of correlation and the bottom number represents the p-value. The lower the p-value the stronger the linear association. The Pearson's coefficient, numbers closer to 1 represents a positive linear relationship, -1 a negative linear relationship, and 0 no linear relationship.

In Table 3, none of the vehicle classes are significantly linearly associated with the NO_x reduction. Furthermore vehicle classes, as the only parameter, did not fully explain the NO_x reduction. From Table 3, the strongest linear correlation is a weak negative correlation between the NO_x reduction and MOVES source 31, the passenger truck, with a p-value of 0.0023. Therefore, when the uncoated area had higher passenger trucks recorded compared to the photocatalytic area, the NO_x reduction was decreased. Unfortunately, this is not logical suggesting that there is another significant parameter that was not accounted in the model.

In Table 4, the correlation coefficients for the speed on the NO_x reduction are reported. None of the parameters are significantly linearly associated with the NO_x reduction. The results of the correlation between all of the parameters combined also showed no correlation. As a result, this suggests that the vehicle emissions are not the main source of pollution for this field study. This is further supported by the MOVES results, which predicted very low amounts of NO_x emitted.

Conclusions

The objective of this study is to evaluate the effects of vehicle activities and classification on NO_x pollution emitted and to correlate this factor to the NO_x reduction from photocatalytic pavements. To achieve this objective, a field study was conducted with 22.3 m^2 of photocatalytic spray coated area and 22.3 m^2 of uncoated control area. Evidence of the photocatalytic reduction of NO_x was evaluated by directly measuring NO_x reductions from the air. A traffic study was conducted for the photocatalytic control areas to characterize the variability in traffic classification and activity between the two areas and its effects on interpreting NO_x reduction. Based on the results of this study, the following conclusions were drawn:

1. The highest amount of NO_x emitted in either the control or the photocatalytic area due to traffic was predicted by MOVES to be no more than 5 grams over an hour period. Therefore, NO_x pollution emitted from the vehicles in this area is not a significant pollution source.
2. Due to the low values of pollution emitted in the both the photocatalytic area and the control area, minor differences in traffic activity between these two areas resulted in significant differences in the amount of pollution emitted between the photocatalytic and the control areas. This may complicate the interpretation of the NO_x reduction results.
3. There was no significant linear correlation of vehicle class and speed and NO_x reduction.

This study provides valuable insight on conducting photocatalytic field studies during a time in which when many state agencies are developing field studies of their own. While previous studies by researchers have shown evidence of the photocatalytic degradation of NO_x based on nitrate surface measurements, further research is still needed to identify relationships between environmental parameters in the field and their effects on NO_x photocatalytic degradation. In spite of the inconclusive results, valuable lessons were learned, which could improve future photocatalytic field studies. First, the field study area should be in an area where traffic pollution is determined as a major source of pollution. Second, the control area and photocatalytic area should be in an area that minimizes variability in traffic activity. In addition, the development of theoretical kinetic studies, which may provide an alternative avenue to understanding the significance of NO_x reduction in field studies through chemodynamic modeling, is needed.

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