Gulf Coast Research Center for Evacuation and Transportation Resiliency

LSU / UNO University Transportation Center

Field and Laboratory Investigation of Photocatalytic Pavements

Final Report

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GULF COAST RESEARCH CENTER FOR EVACUATION AND TRANSPORTATION RESILIENCY

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16. Abstract:

In spite of the importance of the national transportation network, there is a growing recognition that highway operations have major environmental impacts during construction and service. High traffic volumes cause high concentration of nitrogen oxides and VOCs in the air, which have been linked with serious health hazards to the public. These pollutants may also travel long distances to produce secondary pollutants such as acid rain or ozone. Photo-catalysis compounds such as titanium dioxide (TiO2) can trap and degrade organic and inorganic particles in the air removing harmful air pollutants such as NOx and VOC in the presence of UV light. Current research and applications of this technology are limited to concrete pavement surfaces, which only represent 6% of the national road network. About 94% of the road network in the US is surfaced with hot-mix asphalt, which supports directing future research towards the use of titanium dioxide coating in flexible pavements. To address the aforementioned problem, this research project will investigate the possibility of integrating titanium dioxide on the surface of asphalt pavements to develop a photo-catalytic asphalt pavement capable of oxidizing traffic pollutants. The photo-catalytic properties of TiO2 asphalt pavement as well as its environmental properties will be characterized using a novel environmental laboratory setup. The proposed research is cutting edge and has not been attempted in the US. A recent study attempted to apply the photo-catalytic compound as part of a water-based emulsion in Italy. The mixing of TiO2 with an asphalt binder at a 6% content of the binder weight was also attempted in China and was used in the construction of an open-graded friction course.

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Table of Contents

EXECUTIVE SUMMARY 1
ABSTRACT 2
1.0 INTRODUCTION 3
2.0 OBJECTIVES 3
3.0 BACKGROUND 4
3.1 USE OF TIO_2 IN PAVEMENT APPLICATIONS 4
3.2 MEASUREMENTS OF FIELD EFFICIENCY 6
4.0 METHODOLOGY 7
4.1 FIELD PHOTOCATALYTIC SPRAY COAT APPLICATION 7
4.2 NO_X AMBIENT AIR DETECTION 9
4.3 FIELD SAMPLING OF NITRATE 10
4.3.1 Nitrate Laboratory Determination 11
4.3.2 Laboratory Testing 12
5.0 RESULTS AND ANALYSIS 13
5.1 CONCRETE TEST SITE 13
5.1.1 Variation of NO_x Reduction with Environmental and Operating Variables 14
5.2 ASPHALT TEST SITE 17
5.3 NITRATE ANALYSIS 20
5.3.1 Coating Field Durability 21
5.3.2 Comparison of Field and Laboratory NO Removal Efficiency 22
6.0 SUMMARY AND CONCLUSIONS 23
7.0 RECOMMENDATIONS 24
8.0 OUTCOMES 24
9.0 REFERENCES 25

Table of Figures

FIGURE 1: Illustration of the Photocatalytic Process……………………………………………5

FIGURE 2: TiO_2 Photocatalytic Coating Field Application……………………………………...8

FIGURE 3: Equipment used for Field Data Collection…………………………………………..9

FIGURE 4: Weather Station and Traffic Counter………………………………………………10

FIGURE 5: Sampling of Nitrate on Photocatalytic Pavement Coating…………………………10

FIGURE 6: Standard Calibration Curve to Determine Nitrate Concentration Based on the Colorimetric Method……………………………………………………………………………..11

FIGURE 7: Laboratory Experimental Test Setup………………………………………………..12

FIGURE 8: Typical Variation of NO_x Concentration during Laboratory Experiment…………13

FIGURE 9: Daily NO_x Reduction…………………………………………………………………14

FIGURE 10: Variation of Average Hourly NO_x Reductions with Traffic Level………………..14

FIGURE 11: Variation of Average Hourly NO_x Reduction with Relative Humidity…………...15

FIGURE 12: Variation of Average Hourly NO_x Reduction per Solar Radiation………………15

FIGURE 13: Daily Variation of Average NO_x Reduction Corresponding to Daily Variation of Solar Radiation……………………………………………………………………………………...16

FIGURE 14: Variation of Average Hourly NO_x Reduction with Wind Speed…………………16

FIGURE 15: Variation of Average Hourly NO_x Reduction (ppb) with Wind Direction………..17

FIGURE 16: NO Concentration Reduction Efficiency in the Field……………………………..18

FIGURE 17: Nitrogen Oxide (NO) – Before Application………………………………………19

FIGURE 18: Nitrogen Oxide (NO) – After Application………………………………………...19

TABLE 1: Descriptive Statistic of the Developed Models……………………………………...19

FIGURE 19: Nitrogen Oxide (NO) Reduction Efficiency………………………………………20

FIGURE 20: Nitrate Concentrations during the Seven-Day Collection Cycle…………………21

FIGURE 21: NO Removed in the Treated Section during the Seven-Day Collection Cycle……21

FIGURE 22: Comparison of NO reduction 48 hours after Application and Six Months after Application……………………………………………………………………………………….22

FIGURE 23: Comparison of NO Removal Efficiency in the Field and in the Laboratory……...23

Executive Summary

The US faces a significant challenge in controlling air pollution resulting from transportation activities and the growing population density. Validation of the effectiveness of photocatalytic pavements and their implementation in a manner that does not degrade the environment has the potential to expand the use of this sustainable technology to mitigate many of the problems associated with pollution from motor vehicles. The objective of this study was to design and construct a photocatalytic pavement that can purify the air from traffic emissions by oxidizing air pollutants including Nitrogen Oxides (NOx). To achieve this objective, a full-scale existing road segment was treated and monitored for the duration of the project. To characterize the by-products of the photocatalytic reaction, water runoff samples were collected regularly from the side of the pilot test section. The chemical compositions of by-products were determined and were compared to the chemical compositions of the water run-off obtained from an untreated nearby site.

Hassan and co-workers laid the country's first air-purifying asphalt and concrete photocatalytic pavements on Dec. 20, 2010. The test area is a pavement site located on LSU campus. NOx concentrations were monitored for both the coated and uncoated sections for three weeks during the spring season to directly measure photocatalytic degradation. Further, nitrates were collected from the coated and uncoated areas for evidence of photocatalytic NOx reduction.

Results of the direct method and indirect methods of measuring photocatalytic degradation of NOx show that there is evidence of a photocatalytic reaction occurring in the field. The photocatalytic process is very active during the first four days followed by a slight decrease in degradation rate of NOx. Full regeneration of photocatalytic activity takes place in the field through a self-cleaning process during rain event. Six months of traffic and in-service operating conditions did not affect the efficiency of the photocatalytic coating as compared to its efficiency just after installation. In addition, there was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation and in the laboratory experiment at the same level of relative humidity. Results identified that relative humidity, wind speed and direction, light intensity, and solar radiation have a strong impact on photocatalytic degradation efficiency. However, due to the variability demonstrated in the results, additional factors such as vehicle activity and vehicle classification need to be evaluated. The fact that the pilot road segments covered in this study were treated after construction shows the potential of this new technology in improving the environmental conditions in the vicinity of millions of miles of paved roads in the US. Once established, the technology has potential of getting adopted in new pavement construction.

Abstract

In spite of the importance of the national transportation network, there is a growing recognition that highway operations have major environmental impacts during construction and service. High traffic volumes cause high concentration of nitrogen oxides and VOCs in the air, which have been linked with serious health hazards to the public. These pollutants may also travel long distances to produce secondary pollutants such as acid rain or ozone. Photo-catalysis compounds such as titanium dioxide (TiO2) can trap and degrade organic and inorganic particles in the air removing harmful air pollutants such as NOx and VOC in the presence of UV light. Current research and applications of this technology are limited to concrete pavement surfaces, which only represent 6% of the national road network. About 94% of the road network in the US is surfaced with hot-mix asphalt, which supports directing future research towards the use of titanium dioxide coating in flexible pavements. To address the aforementioned problem, this research project will investigate the possibility of integrating titanium dioxide on the surface of asphalt pavements to develop a photo-catalytic asphalt pavement capable of oxidizing traffic pollutants. The photo-catalytic properties of TiO2 asphalt pavement as well as its environmental properties will be characterized using a novel environmental laboratory setup. The proposed research is cutting edge and has not been attempted in the US. A recent study attempted to apply the photo-catalytic compound as part of a water-based emulsion in Italy. The mixing of TiO2 with an asphalt binder at a 6% content of the binder weight was also attempted in China and was used in the construction of an open-graded friction course.

1.0 Introduction

The importance of the national transportation network to the US economy is indisputable; however, there is a growing recognition that highway construction and maintenance have major environmental impacts (1, 2). Road microenvironments contribute 29% of the volatile organic compounds (VOCs), 35% of the nitrogen oxides (NO_x), and 58% of the carbon monoxide (CO) emitted in the US (1, 3). These concentrations are often higher in cities where trends of urban development and increase in traffic volumes add to emissions while street canyon conditions inhibit their dispersion resulting in high ground level pollutant concentrations. The emissions of harmful air pollutants associated with highway operations often surpass the concentrations from industrial sources making traffic emissions the primary source of urban air pollution (4-7). Consequently, many adverse health effects are being linked to areas within 100 m from roads where pollution is not fully diluted, which affects more than 35 million Americans who live within this proximity limit. Thus transportation pollution is considered a major concern (5).

The mobile nature of vehicle pollution sources significantly impacts how much emissions are emitted and the extent of the associated negative impact imposed on society. Consequently, the success of efficiently reducing traffic emissions is difficult. Increasing fleet size persistently offsets the vehicle emission reductions. As a result, EPA expects that regulations will continually get stricter (8). Some researchers argue that this practice of continually reducing the emissions from vehicles through improved technology may not be enough (9). Thus, a solution to reduce vehicle emissions once they are emitted into the atmosphere is needed.

Many organic compounds and air pollutants including nitrogen oxides and sulfur oxides can be decomposed by ultraviolet (UV) radiation but this process is extremely slow. Using heterogeneous photocatalysis, pollutants emitted into the atmosphere are decomposed to nonhazardous waste products with little energy requirements and little selectivity (10, 11). Photocatalytic pavements reduce pollutants such as NO_x by 40 to 85% once pollutants are emitted in the air (12). 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. As a result, many field studies are underway to demonstrate the potential of photocatalytic pavements under real world conditions. However, quantification of nitrogen oxides reduction in field studies is difficult and challenging due to the large number of environmental and operating variables (13).

2.0 Objectives

This project aims to evaluate the concept of designing and constructing a photocatalytic pavement that can purify the air from traffic emissions by oxidizing air pollutants including Nitrogen Oxides (NOx). To achieve this objective, a full-scale existing road segment was treated and monitored for the duration of the project. To characterize the by-products of the photocatalytic reaction, water runoff samples were collected regularly from the side of the pilot test section. The chemical compositions of the by-products were determined and were compared to the chemical compositions of the water run-off obtained from an untreated nearby site. It was the country's first air-purifying photocatalytic asphalt and concrete pavements to the knowledge of the authors.

3.0 Background

Initial interest in environmental photocatalysis began in the 1970s, initiated by Fujishima and Honda's research in photo-electrochemical solar energy conversion. Through biomimicry of plant photosynthesis, the researchers attempted to replicate the photo-induced redox reactions, by oxidizing water and reducing carbon dioxide, using a semiconductor irradiated by UV light (14). Since then, increased interest in environmental photocatalysis was observed, which caused TiO_2 to be applied to glass, tile, paper, and pavements for self-cleaning materials, water purification, air purification, sterilization, and oil spill remediation. From these studies, it has been shown that organic and inorganic compounds can be completely decomposed and that the TiO_2 surface has the ability to self-regenerate (15). Therefore, rather than absorbing pollutants, which is common to traditional air purification methods, heterogeneous photocatalysis can decompose pollutants to nonhazardous waste products with little energy requirements (10). In the presence of UV light, TiO_2 produces hydroxyl radicals and superoxides, which are responsible for oxidizing and reducing environmental contaminants including VOCs and NO_x (16). A proposed mode of oxidation of NO_x via hydroxyl radical intermediates in the presence of the photocatalyst is described by the following equations:

$$NO + \dot{O}H \xrightarrow{T_iO_2} NO_2 + H^{\cdot} \qquad (1)$$

$$NO_2 + \dot{O}H \xrightarrow{T_iO_2} NO_3 + H^{\cdot} \qquad (2)$$

Based on this heterogeneous photocatalytic oxidation process, NO_x are oxidized into water-soluble nitrates; these substances can be washed away by rainfall.

3.1 Use of TiO_2 in Pavement Applications

The mechanism described in Equations (1) and (2) through which TiO_2 accelerates the decomposition of air pollutants such as NO_x from air in the presence of UV light is shown in Figure 1. TiO_2 photocatalytic technologies in pavement applications have been mostly directed towards concrete pavements by applying a photocatalytic concrete overlay, a thin exterior film of suspended TiO_2 nanoparticles in a binding agent (cement), or by sprinkling TiO_2 nanoparticles on curing concrete (17, 18). Researchers prefer photocatalytic overlays due to their greater durability (19, 20). Nonetheless, the spray coating application has the advantages of being easy to construct and potentially cheaper to apply to existing pavements.

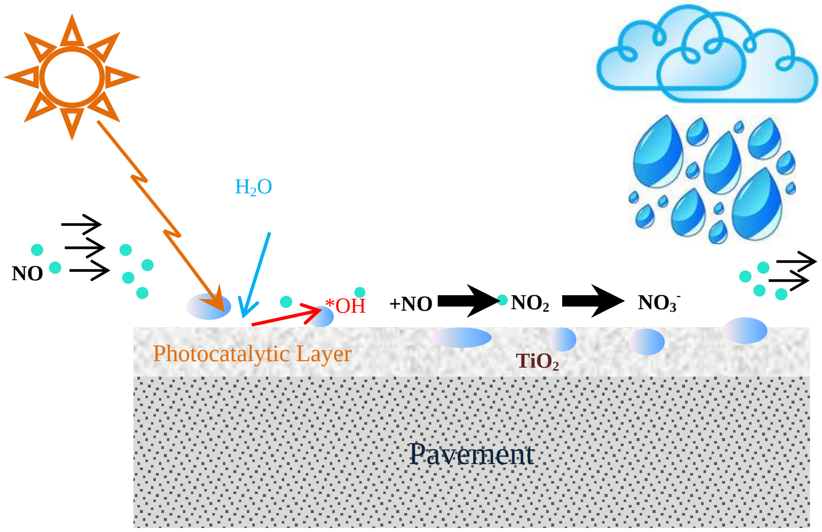


FIGURE 1: Illustration of the Photocatalytic Process

Research results by Hassan and co-workers in recent years have measured the impact of common roadway contaminants including motor oil, dirt, and de-icing salt on the effectiveness of photocatalytic roadways' ability to remove NO_x from the atmosphere (21). Results of the experimental program showed that the three contaminant types had a strong negative impact on the photocatalytic NO_x removal efficiency. The impact of contaminants' coverage was largely dependent on the soilure type with oil having the largest negative impact. An increase in the flow rate and air relative humidity also resulted in lower NO_x efficiencies. Hassan and co-workers evaluated the environmental effectiveness of TiO_2 coating in photodegrading mixed NO_2 and NO gases from the atmosphere (22). Results of the experimental program determined that increasing the flow rate and NO_2/NOx ratio negatively affect the effectiveness of the photocatalytic process. However, the extent of this impact depends on many other factors including flow rate.

Few studies attempted to use TiO_2 in asphalt pavements (23, 24). In Italy, TiO_2 has been incorporated into asphalt pavements as a thin surface layer that is sprayed on existing pavements (23). The water-based emulsion was applied by two different methods, referred to as hot and cold method; distinguished by the spraying of the emulsion during asphalt paving laying operations when the pavement temperature is over 100°C or on existing pavements at ambient temperatures (23). The study results showed that the reduction efficiencies were highly dependent on the type of TiO_2 nanoparticles used with NO_x reduction efficiency ranging from 20 to 57%. Meanwhile, researchers in China mixed TiO_2 with an asphalt binder at a 2.5% content of the binder weight to an emulsified asphalt pavement (24). Evaluation presented in this study showed that a maximum efficiency in removing nitrogen oxide near 40% was achieved. A more efficient approach may be achieved by concentrating the photocatalytic compound at the pavement surface.

3.2 Measurements of Field Efficiency

To measure the pollution reduction of NO_x continuously in the field often presents a challenge, due to a large number of influencing parameters, time, and costs. Despite the amount of field studies, Hunger et al. highlight that none of the current field studies demonstrate a reduction in pollution exclusively resulting from the photocatalytic pavements (25). Nonetheless, it is agreed that photocatalytic field studies are the next step to advance the use of photocatalytic pavements. Two techniques to measure photocatalytic degradation from field studies have been explored. 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 the byproducts created from the degradation process.

Of the many pollutants present in roadway microenvironments, nitrogen oxides are the most commonly used pollutant to evaluate the reduction of photocatalytic pavements. Nitrogen oxides, emitted from vehicle combustion, are easy to monitor in the air and the photocatalytic byproduct nitrates can also be measured. Further, roadway microenvironments contribute to 58% of NO_x emissions, which have detrimental effects on the outdoor environment by promoting acid rain and on indoor air quality, contributing to sick building syndrome (26). To directly measure NO_x reductions from photocatalytic roadways, the approved method of ambient air NO_x detection is chemiluminescence. Chemiluminescence occurs when light is emitted from a reaction, which in the case of NO_x is between NO and ozone. The amount of light emitted is proportional to the NO concentration. For nitrogen dioxide, an indirect approach is taken, since a catalytic converter must first reduce the nitrogen dioxide to nitric oxide in order to be measured. After catalytic conversion, the total NO measured corresponds to the NO_x concentration. Therefore, the nitrogen dioxide concentration is the difference between the total NO_x and the NO (27, 28). Another technique used to monitor ambient NO_x concentrations is to trap the gaseous pollutants onto a filter in which the concentrations are determined using laboratory colorimetric methods (29).

Field studies have attempted to quantify NO_x reduction using chemiluminiescent ambient air monitoring techniques. Simultaneous measurements are preferred to compare photocatalytic pavement areas and non photocatalytic pavement areas under similar environmental conditions. Li and Qian (2009) used this technique and measured NO_x reduction for 1 hour a day of each month illustrating a photocatalytic reaction occurring in the field with reductions as high as 80% (24). Field studies using traps concluded up to 16% reductions (20). However, long-term continuously monitored data has not been reported and is necessary to understand the full potential of photocatalytic pavement under various environmental conditions. These environmental conditions not only impact the photocatalytic reduction efficiency but also interfere with pollutants dispersion (30).

Pilot studies have been used as an intermediate step between laboratory and full-scale tests in order to eliminate the additional factor of pollutants dispersion. A pilot study in France controlled the pollution source concentration and pollution distribution to evaluate the photocatalytic reductions from coated artificial street canyon walls under various environmental conditions. The first period measured the street canyon pollution from panels treated with a photocatalytic mortar and the second period was used to measure pollution from panels with no coating. The ambient air background concentrations were measured and subtracted from the total emissions measured. The difference between the coated and control average concentrations was then used to calculate photocatalytic degradation efficiency of NO_x (13). Results concluded that NO_x could be reduced with an efficiency ranging from 36 to 82% dependent upon the pollution emissions, wind direction, and wind speed (13). However, having a constant, uniform distribution of pollution is not likely in field applications where vehicle activity is variable.

The second technique is to use indirect techniques to measure photocatalytic reductions. For NO_x, the indirect method evaluates the photocatalytic degradation of NO_x by measuring the NO_3 deposited on the surface. Nitrates are water-soluble and therefore washed from the surface with water to be quantified (20). By knowing the amount of NO_3 collected, the amount of degradation is indirectly calculated, using the stoichiometry given in Equations (1) and (2). Beeldens (2008) used indirect technique to measure the photocatalytic degradation of NO_x from removable pavement blocks (20). Results illustrated that 2 mmol NO_x/m^2 can be removed in 12 hours. However, results recorded in the field were unable to develop any photocatalytic reduction relationships due to the numerous impacting factors (i.e. traffic activity, wind, light, and humidity making comparisons difficult) and given that nitrate ions were not completely eluted (20, 30).

The objective of this study is to identify evidence of photocatalytic reductions and to identify the significant factors impacting photocatalytic reductions in efforts to advance the results of future field studies. To achieve this objective, a field study was conducted and the photocatalytic reduction was directly and indirectly measured for NO_x. In addition, the experimental program monitored significant environmental and operating factors during the test period.

4.0 Methodology

4.1 Field Photocatalytic Spray Coat Application

The photocatalytic spray coat used was a mixture of TiO_2 anatase nanoparticles with an average size of 6 nm suspended in an aqueous liquid at 2% by volume. Before application, the roadway was cleared of any debris. A primer was applied first before the photocatalytic coat. A distributor truck was used for the application process. Mounted on the back of the truck, a spray bar fitted with nozzles distributed TiO_2 water-based solution at the specified application rate, 1.5 to 2.0 ml/ft^2 (Figure 2). The application rate was adjusted by altering the truck speed and nozzle type and size. Further, the nozzles had electrostatic precipitators to separate the TiO_2 nanoparticles suspended in the aqueous solution and to ensure a more even coverage.

Concrete Pavement Application

Asphalt Pavement Application

FIGURE 2: TiO_2 Photocatalytic Coating Field Application

4.2 NO_x Ambient Air Detection

To characterize the test location and to build a baseline case for comparison, field data including NO, NO_2, NO_x concentrations, traffic count and classification, and climatic conditions were monitored and recorded for a month prior to TiO_2 field application. After application, monitoring and recording of the field data was continued for an additional month to quantify the reduction in NO_x under different conditions. After five months of application, the same field data were collected to quantify the reduction in efficiency and to compare it with the efficiency recorded right after application as an indication of short-term durability of the coating.

Equipment used for field data collection was housed in an air-conditioned trailer. A Thermo 42i NO_x analyzer was used for monitoring NO, NO_2 and NO_x concentrations as shown in Figure 3a. The NO_x analyzer was calibrated in accordance to EPA calibration procedures using the gas phase titration (GPT) alternative. A Thermo 146i gas calibrator was used for calibration of the NO_x analyzer. The NO_x analyzer was calibrated at five different spans for NO calibration and four different ozone settings for NO_2 calibration to confirm linearity and ozone converter efficiency. In addition, the air-conditioned trailer was located next to a Department of Environmental Quality (DEQ) air monitoring station as can be seen in Figure 3b. The DEQ station records ambient air NO_x, NO, NO_2, VOC and Ozone levels. Data from the station was used to supplement data collected in this study. After calibration, the NO_x analyzer was connected to ambient air at the pavement level using a stainless steel perforated pipe placed in the middle lane as shown in Figure 3c. Stainless steel was chosen because it is non-reactive.

(a) NO_x analyzer and calibrator **(b) DEQ station**

(c) Air Sampling Pipe
FIGURE 3: Equipment used for Field Data Collection

To monitor climatic conditions at the site, a Davis Vantage Pro2 weather station was installed in the field that recorded and stored meteorological data including humidity, ambient temperature, wind speed, wind direction, rain, dew point, and solar radiation continuously each minute as shown in Figure 4a. As for operating conditions, a traffic counter was installed to count and classify the number of vehicles per minute per lane as shown in Figure 4b.

(a) Weather Station **(b) Traffic Counter**

FIGURE 4: Weather Station and Traffic Counter

4.3 Field Sampling of Nitrate

The concentration of nitrates was measured in six predefined locations, three in the coated area and three in the uncoated area. Measurements were collected for three consecutive days during the study to identify evidence of photocatalytic degradation of NO_x. Nitrates accumulated on the pavement surface were measured by dissolving them in deionized (DI) water. To collect the nitrate on the pavement surface, 40 mL of DI water was poured into a 100 mm x 150 mm rectangle opening in a wooden device sealed with plumber putty as shown in Figure 5. After five minutes, the solution was collected via a syringe and filtered through a 0.45 μm filter into a polyethylene jar. Three samples were collected from both the coated and uncoated areas and transported to the laboratory for immediate analysis. An increase in nitrates on the coated pavement would demonstrate evidence of photocatalytic reduction of NO_x.

FIGURE 5: Sampling of Nitrate on Photocatalytic Pavement Coating

4.3.1 Nitrate Laboratory Determination

Field samples were immediately transported to the laboratory for analysis and nitrate quantification. To quantify nitrate concentration in the collected samples, the colorimetric method of cadmium reduction with a Shimadzu UV Spectrophotometer 1800 was adopted (31). In this method, the cadmium metal is used to convert nitrite ions from nitrates into nitrites, which then reacts with a reagent (chromotropic acid) to form a pink-colored solution. The intensity of color in the solution is proportional to the concentration of nitrate in the sample. The color intensity is measured by means of a UV Vis Spectrophotometer by measuring the amount of light absorbed at a 507 nanometer wavelength. The light absorption is then correlated to nitrate concentration by means of a standard calibration curve. An example of a calibration curve developed in this study to relate light absorption counts to nitrate concentration is presented in Figure 6.

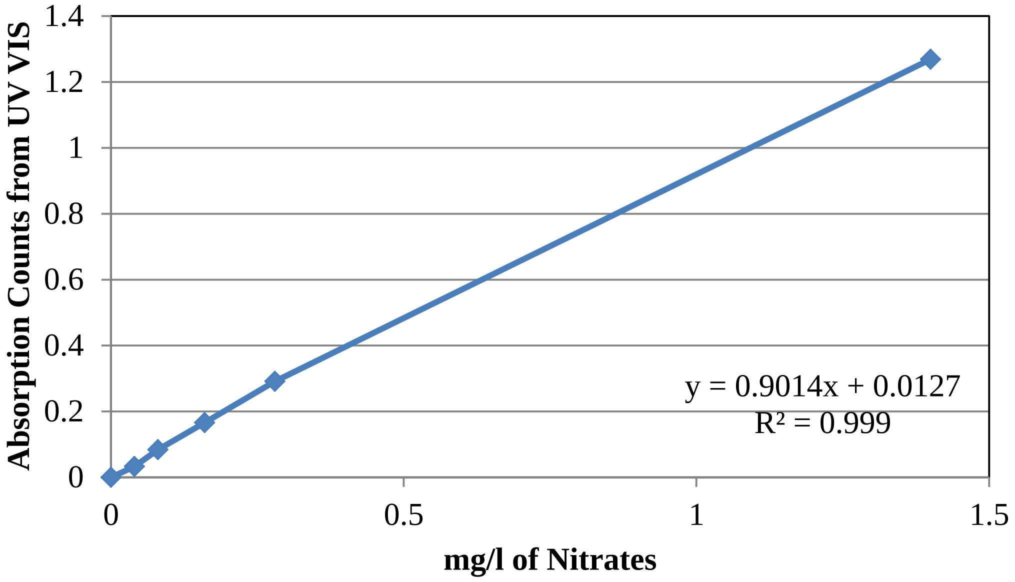


FIGURE 6: Standard Calibration Curve to Determine Nitrate Concentration Based on the Colorimetric Method

Given the direct relationship and mole equivalency between the oxidized nitrogen oxides and the deposited nitrates on the pavement surface (see Equations 1 and 2), the measured concentration of nitrates may be used to backcalculate the volume of pollutants oxidized in the atmosphere (ppmV). The EPA conversion method used in this analysis is summarized as follows (32):

1. **Step 1**: Convert nitrate concentration from mg/l to mole of NO/l knowing the molecular weight of NO_3 and NO;
2. **Step 2**: Convert NO concentration from mol NO/l to mass of contaminants in g NO/l;
3. **Step 3**: Determine volume of NO contaminant in liter based on the ideal gas law as follows:

$$V_{contaminant}\ [L] = \frac{Mass_{contaminant}[g]}{Molecular\ Weight_{contaminant}\left[\frac{g}{mol}\right]} \times 8.3144 \left[\frac{L.kPa}{mol.K}\right] \times T_{air} \times \frac{1}{P_{air}[kPa]} \quad (3)$$

where,
$V_{contaminant}$ = volume of NO contaminant in liter;
$Mass_{contaminant}$ = determined from Step 2;
T_{air} and P_{air} = temperature and pressure of air; and
Other parameters are as previously defined.

4. **Step 4**: Convert volume of NO contaminant from liter to ppmV (ppmV = volume in ml/m^3).

4.3.2 Laboratory Testing

NO removal efficiency determined in the field was compared to nitrogen oxide removal efficiency predicted in the laboratory for the same rate of photocatalytic coating applied one the same concrete substrate. The experimental setup used to collect the laboratory data was modified from the Japanese Industrial Standard (JIS TR Z 0018 "Photocatalytic materials – air purification test procedure") (33), Figure 7.

FIGURE 7: Laboratory Experimental Test Setup

The laboratory procedure calls for each sample to be tested for a total time of eight hours under UV-irradiation that is started after at least 180 minutes to ensure equilibrium concentrations. The environmental efficiency is calculated by analyzing the concentrations of NO, NO_2, and NO_x with the "lights on" compared to the difference in concentrations with the equilibrium at "lights off". Figure 8 illustrates the typical variation of NO_x concentration during the testing process. Testing was conducted at three levels of relative humidity (20, 50, and 80%). More details about the laboratory experimental setup have been presented elsewhere (21). Testing was conducted at room temperature as this is the standard test temperature in the JIS. It is noted in photocatalytic degradation, only large temperature differences such as the difference between summer and winter may affect the photocatalytic reaction with increasing temperatures helping the reaction.

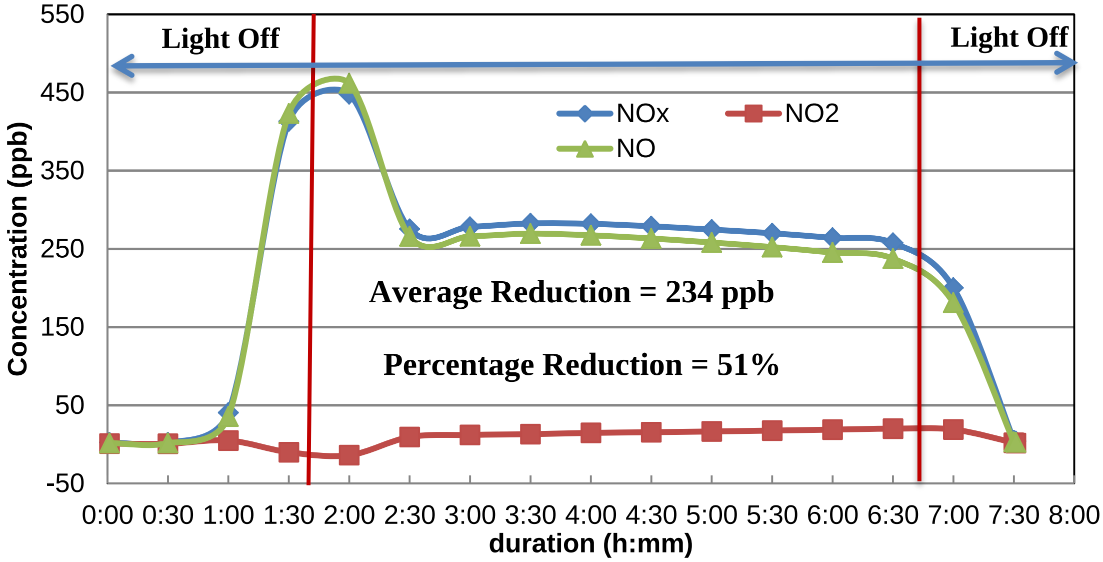


FIGURE 8: Typical Variation of NO_x Concentration during Laboratory Experiment

5.0 Results and Analysis

5.1 Concrete Test Site

Measuring the pollution reduction of NO_x continuously in the field often presents a challenge, due to a large number of influencing parameters, time, and costs. In order to limit the variation due to environmental parameters, NO_x concentrations were measured simultaneously for the coated and uncoated section, eliminating variables such as humidity, temperature, wind direction, and wind speed. However, it should be noted that the traffic count during the 5 minute period was not always equal for the two locations since there was a time lag between the time the car passes the counter and either of the NO_x sample lines. In addition, vehicles may park or idle any time after passing the counter. Nevertheless, the difference between the coated and the uncoated section concentrations theoretically should represent the photocatalytic NO_x reduction. Using this assumption, the daily total NO_x reduction is presented in Figure 9. From the figure, it is evident that the total daily NO_x reduction varies significantly during the day. This illustrates the difficulty in understanding the photocatalytic reductions from field studies. Reduction presented in Figure 9 correlates to approximately 0.019-0.13 mmol NO/m^2 of photocatalytic pavement reduced per day assuming that the reduction measured was from 2.5 cm radius circle around the sampling point.

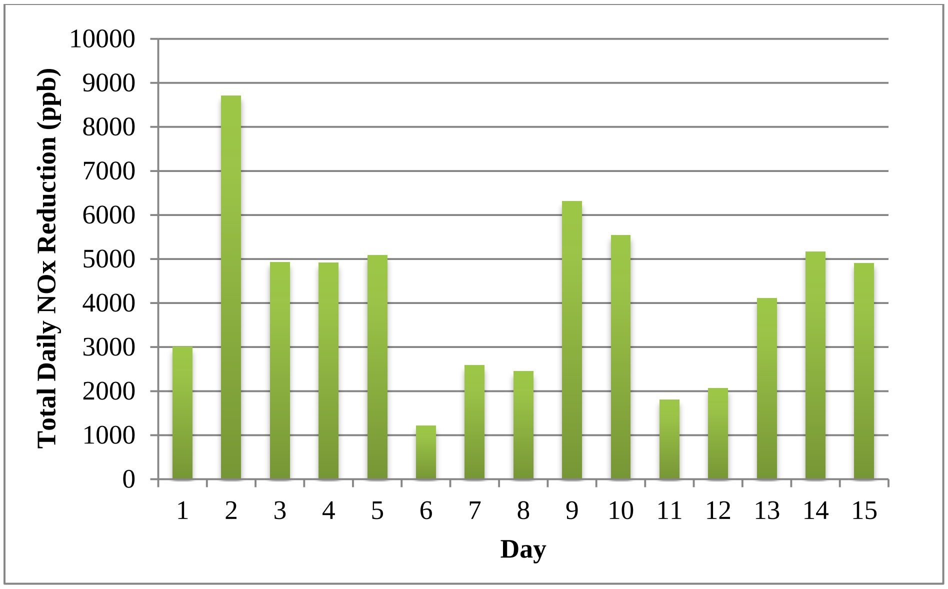


FIGURE 9: Daily NO_x Reduction

5.1.1 Variation of NO_x Reduction with Environmental and Operating Variables

To better understand field NO_x reductions, the effects of environmental parameters were investigated. To identify the influence of these parameters, photocatalytic degradation was plotted against each environmental factor including traffic. Figure 10 illustrates the average NO_x reduction observed over the three week period plotted against its associated traffic count. The variation observed illustrates the influence of numerous factors including wind speed, vehicle type, humidity, and temperature on NO_x dispersion. Furthermore, it should be noted that the field site location had relatively low traffic concentrations explaining the low NO_x concentrations as well.

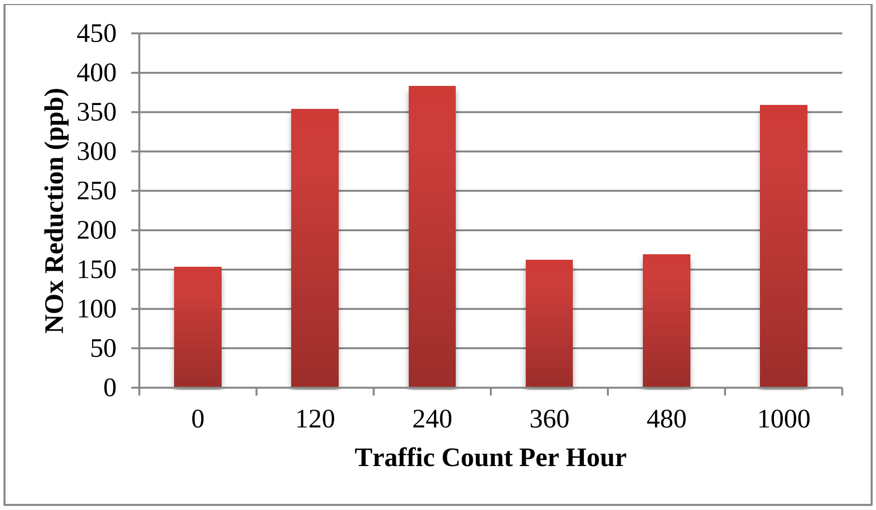


FIGURE 10: Variation of Average Hourly NO_x Reductions with Traffic Level

To evaluate the impact of various environmental parameters, the hourly average NO_x reduction was plotted against known environmental parameters; humidity, solar radiation, wind speed, and wind direction. Despite the impact of other variables, Figure 11 shows a clear trend, as the humidity increases, NO_x reduction decreases. Furthermore, this trend is consistent with previous laboratory studies results, which demonstrated the negative impact of relative humidity (17).

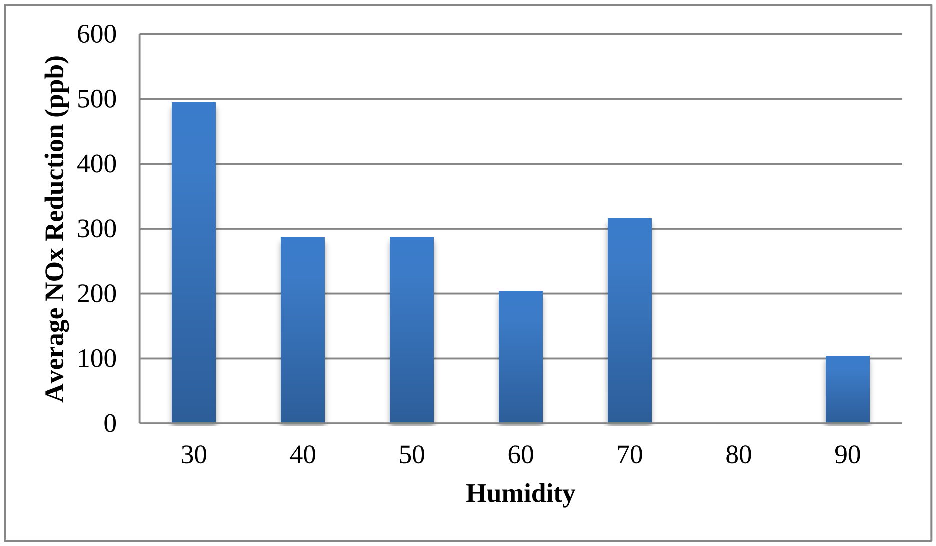


FIGURE 11: Variation of Average Hourly NO_x Reduction with Relative Humidity

Figure 12 illustrates the variation of the hourly average NO_x reduction with solar intensity. As shown in this figure, no clear trend is evident. However, by examining the impact of solar radiation hourly over a period of a day, where the relative humidity and wind speed was more stable, a correlation is evident, see Figure 13. As shown in Figure 13, as the solar radiation increases, the percent NO_x reduction also increases.

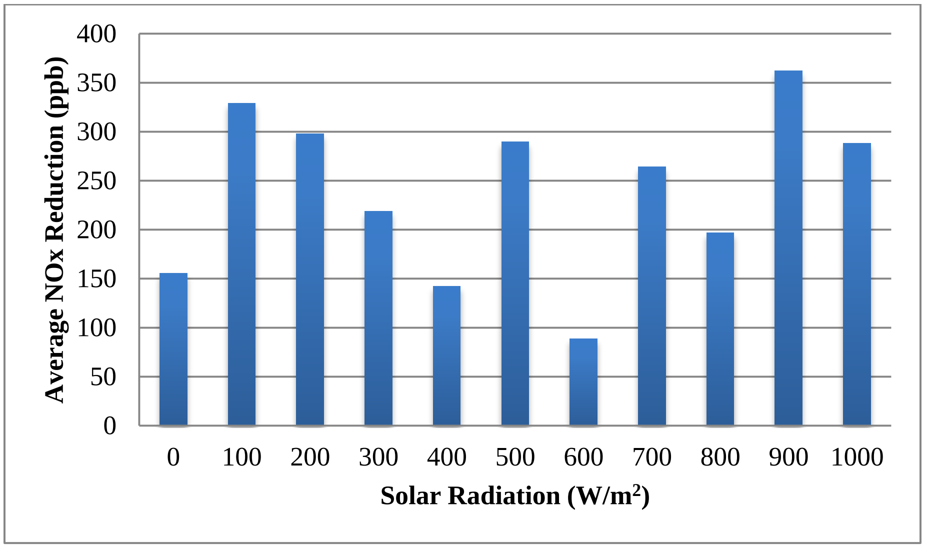


FIGURE 12: Variation of Average Hourly NO_x Reduction per Solar Radiation

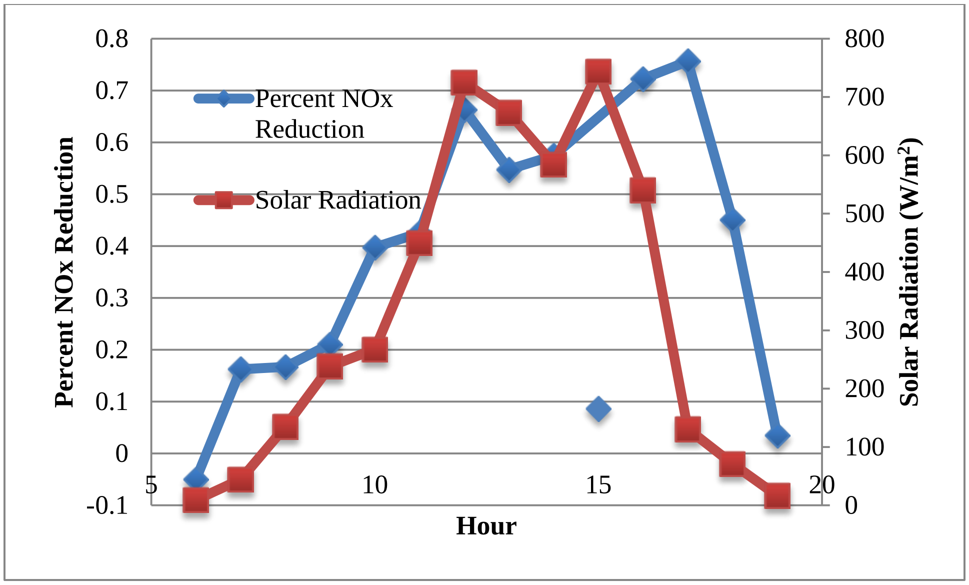


FIGURE 13: Daily Variation of Average NO_x Reduction Corresponding to Daily Variation of Solar Radiation

Figure 14 presents the influence of wind speed on the average NO_x reduction. As shown in this figure, a negative trend is associated with increasing wind speeds. As the wind speed increases, there is less pollutant contact time with the photocatalyst for a reaction to occur, thus the photocatalytic reduction decreases (17).

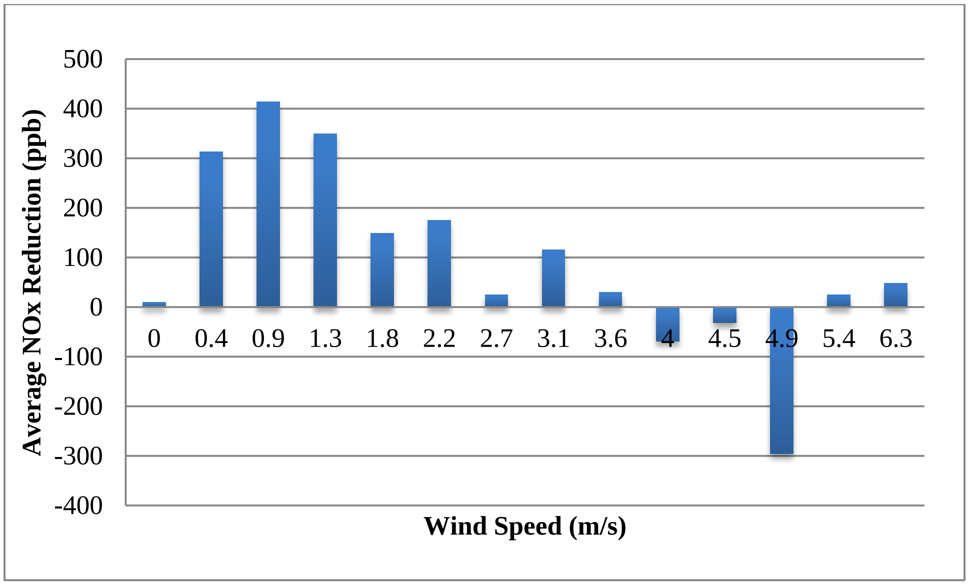


FIGURE 14: Variation of Average Hourly NO_x Reduction with Wind Speed

Figure 15 presents the influence of wind direction on photocatalytic efficiency. The wind direction influences the pollution concentration especially when the direction is downstream from the pollution point source. This may explain the large negative values in the Northeast direction. In addition, the wind direction changes the pollution dispersion characteristics especially as related to the contact time with the photocatalytic coating. For example, Northeast and South-West wind directions are crosswinds compared to the road direction, and therefore, the pollutant contact time with the pavement is lower.

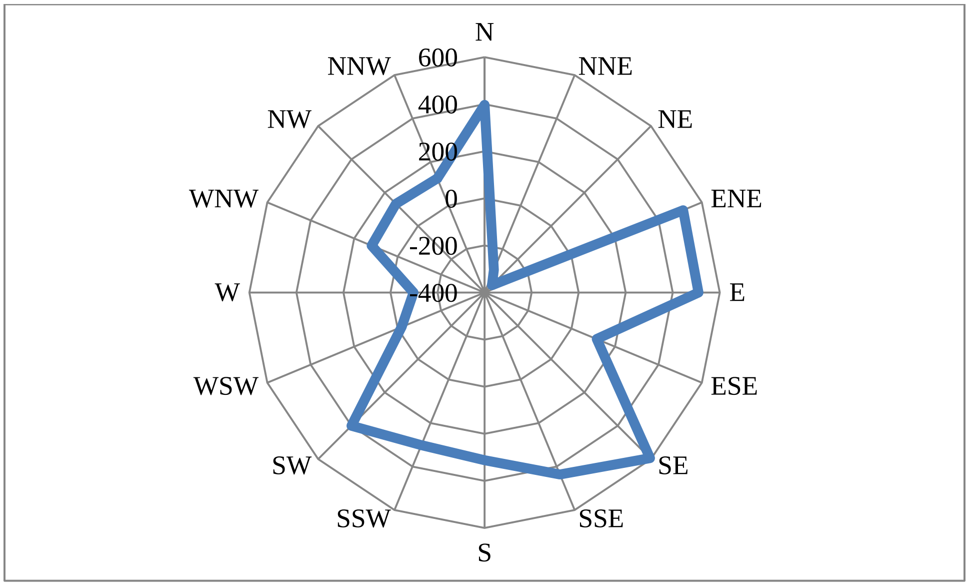


FIGURE 15: Variation of Average Hourly NO_x Reduction (ppb) with Wind Direction

5.2 Asphalt Test Site

Measurements of pollution reduction in the field presented a challenge due to a large number of influencing parameters, time, and costs. In the described field experiment, NO concentration is measured at the pavement level by placing a perforated pipe at the surface in the middle of the lane. Preliminary measurements of NO concentrations in the field showed high variability due to the influence of numerous factors including wind speed, vehicle type, humidity, and temperature. To determine NO reduction efficiency in the field; ten days of data were compared just before and after TiO_2 applications. Figure 16 compares the measured nitrogen oxide (NO) data collected just before and just after application of TiO_2 for several days during the winter season. As shown in this figure, the measured NO concentrations were significantly reduced right after the application of the TiO_2 surface coating on the asphalt pavement. This difference shows the important role of TiO_2 in reducing nitrogen oxide in the environment.

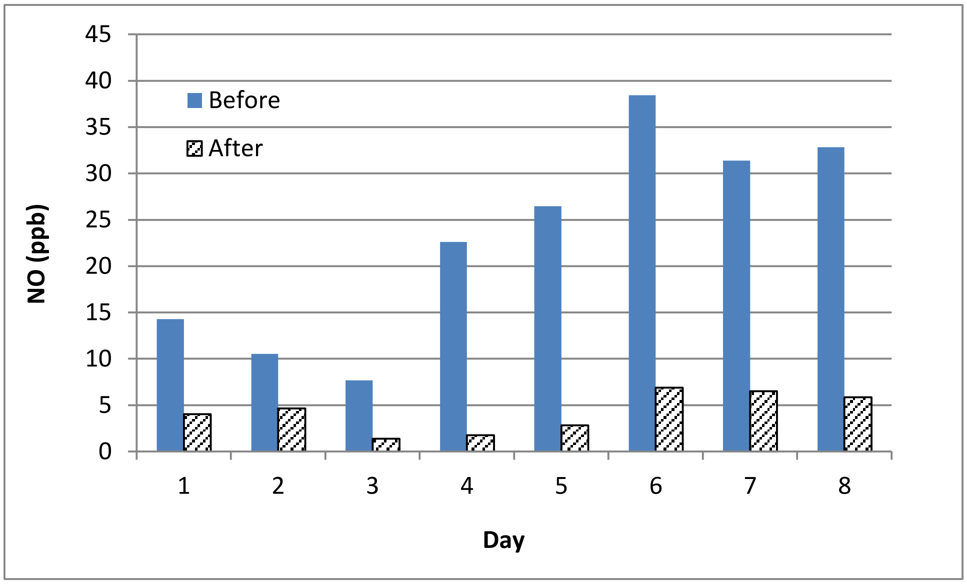


FIGURE 16: NO Concentration Reduction Efficiency in the Field

Due to the limitations in equipment, NO measurements were not conducted concurrently on the treated and untreated sections after TiO_2 application. To address this limitation and to quantify the level of NO concentrations collected under different environmental and traffic conditions, nonlinear regression models were developed for predicting NO concentrations before and after TiO_2 application based on the field data. The regression models were then used to compare NO concentrations with and without TiO_2 under similar operating conditions. The developed regression models relate the measured NO concentration linearly to the operating factors as follows:

$$\text{NO} = f(T, H, V, Tout, S) \tag{4}$$

$$\text{NO}_{\text{Before}} = 0.96{*}\text{T}+0.22{*}\text{H}-1.33{*}\ \text{T}_{\text{out}} -10.5{*}\text{V}+0.02{*}\text{S}$$
$$\text{NO}_{\text{After}} = 0.31{*}\text{T}+0.06{*}\text{H}-0.75{*}\text{V}-0.1{*}\ \text{T}_{\text{out}}+0.0003{*}\text{S}$$

where,
NO = NO concentration at the pavement level in ppb;
T = number of vehicle per hour;
H = relative humidity;
V = wind speed;
T_{out}= outside temperature; and
S= solar radiation

Formulation of the models was divided into two steps: model development and model validation through independent measurements. Statistical goodness of fit was also assessed through the coefficient of determination (R^2) as presented in Table 1. The developed models are only valid in the input ranges shown in Table 1. Based on the measured data, it was found that NO reduction due to photocatalytic pavement should not be expected at a relative humidity greater than 88%.

Table 1: Descriptive Statistic of the Developed Models

Parameters	Range of variation	
	Low Level	High Level
Number of vehicle per hour	2	52
Humidity (%)	31	88
Wind speed (m/s)	0	2.7
Outside temperature (°C)	0	20
Solar Radiation (W/m^2)	0	658
Coefficient of Determination (R^2)	Untreated = 0.79	Treated = 0.67

Figures 17 and 18 compare the measured and predicted NO before and after TiO_2 application, respectively. As shown in these figures, the models successfully respond to the peak increases in NO concentration, which are usually due to the passage of a large vehicle (e.g., bus, truck). However, the model response to regular passenger vehicles was not as timely as it was observed in the measurements. It is noted that environmental variability in NO measurements in the field is around 10 ppb.

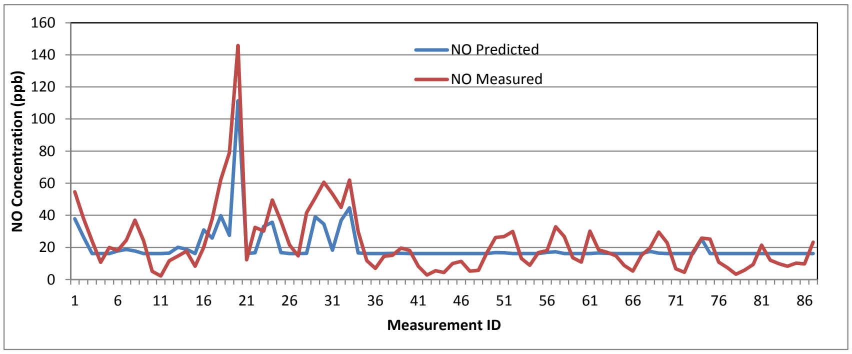


FIGURE 17: Nitrogen Oxide (NO) – Before Application

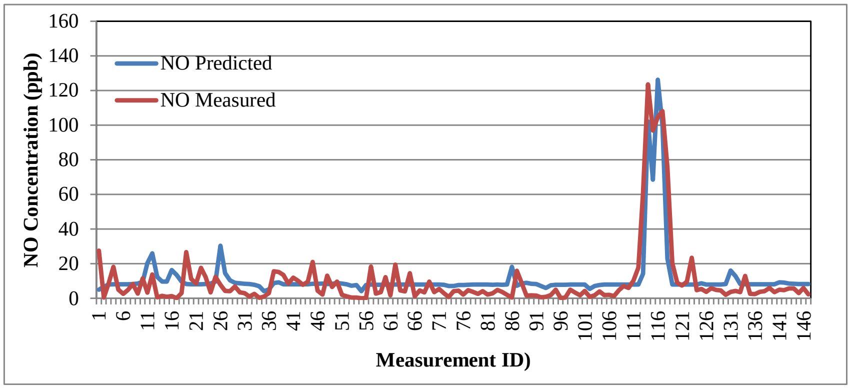
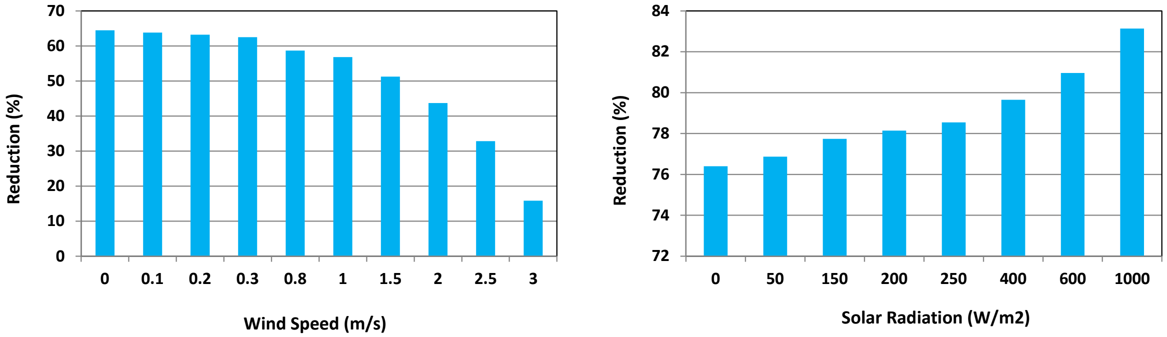


FIGURE 18: Nitrogen Oxide (NO) – After Application

Based on the developed models, Figure 19 shows the NO reduction efficiency due to the photocatalytic coating at different levels of wind speed and solar radiation. As shown in this figure, the maximum NO reduction efficiency was determined at high solar radiation and low wind speed. At high solar radiation (1000 W/m^2), the reduction of NO is approximately 83%. In addition, by changing the wind speed from 0 m/s to 3 m/s NO reduction drops from 62 to 15%. To provide additional insight in the measurements and to assess the durability of the coating, NO$_x$ concentrations will be continuously monitored at the test site at regular time interval to validate these trends.



a. Wind speed effect b. Solar radiation effect

FIGURE 19: Nitrogen Oxide (NO) Reduction Efficiency

5.3 Nitrate Analysis

Figure 20 presents the measured nitrate concentrations throughout the seven-day collection period. Concentrations shown in this figure reflect the concentrations after subtraction of the baseline concentrations measured at the beginning of the collection period. As shown in this figure, there is a definite indication that photocatalytic degradation of nitrogen oxide is taking place in the treated section. The photocatalytic process is very active during the first four days followed by a slight decrease in degradation rate of NO$_x$. It is possible that the accumulation of nitrate at the surface reduced the active sites in the pavement. Full regeneration of photocatalytic activity takes place through a self-cleaning process during rain event. This reduction may also be due to the 5-minutes dilution time used in sample collection, which may need to be increased to ensure that all accumulated nitrate has been collected. Figure 21 presents the backcalculated volume of NO removed in the treated section from the atmosphere based on Equation (3).

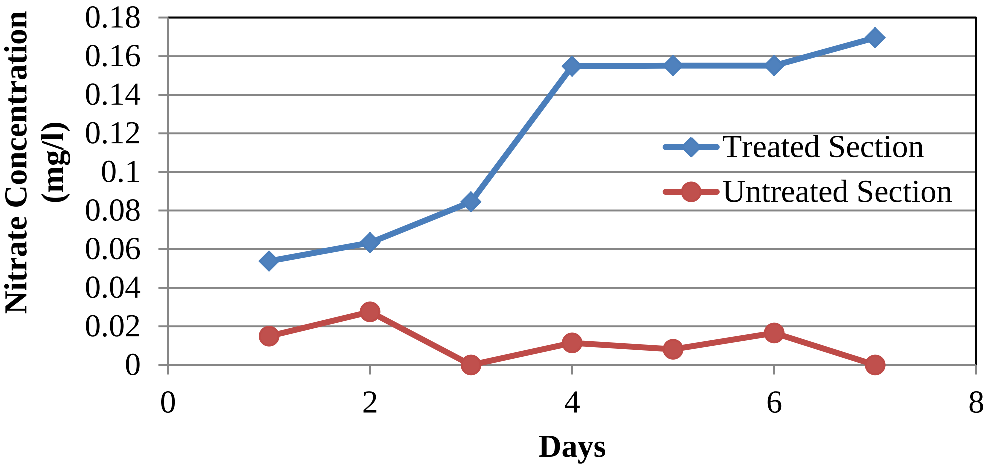


FIGURE 20: Nitrate Concentrations during the Seven-Day Collection Cycle

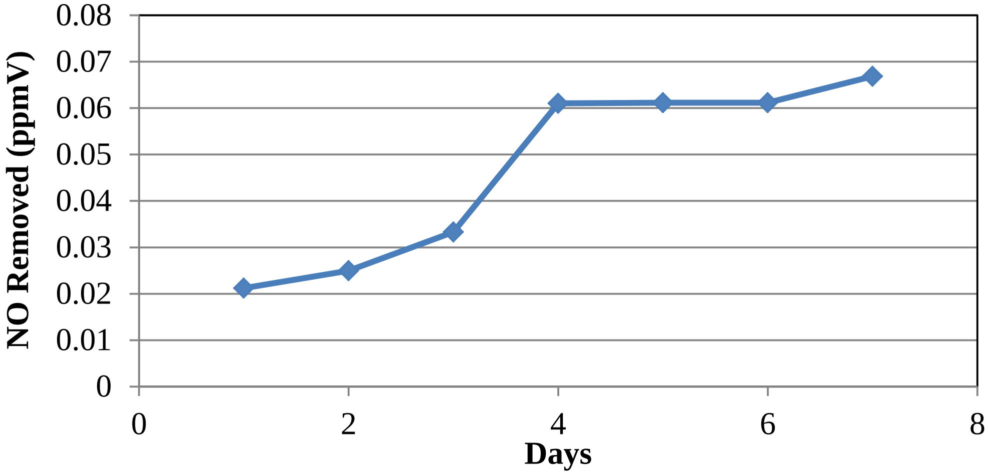


FIGURE 21: NO Removed in the Treated Section during the Seven-Day Collection Cycle

5.3.1 Coating Field Durability

The applied coating has been installed in December 2010. To assess the coating initial durability, the photocatalytic efficiency of the coating was compared 2 days after installation to six months after installation. To compare the efficiency under the same environmental and operating conditions (i.e., traffic, wind, solar radiation, and relative humidity), a small area was recently coated on the traffic lane and on the curb. Nitrate concentrations six months after installation and 2 days after installation are compared on Figure 22. As shown in this figure, six months of traffic and in-service operating conditions did not affect the efficiency of the photocatalytic coating. However, the efficiency of the coating was greater on the curb than in the middle of the lane.

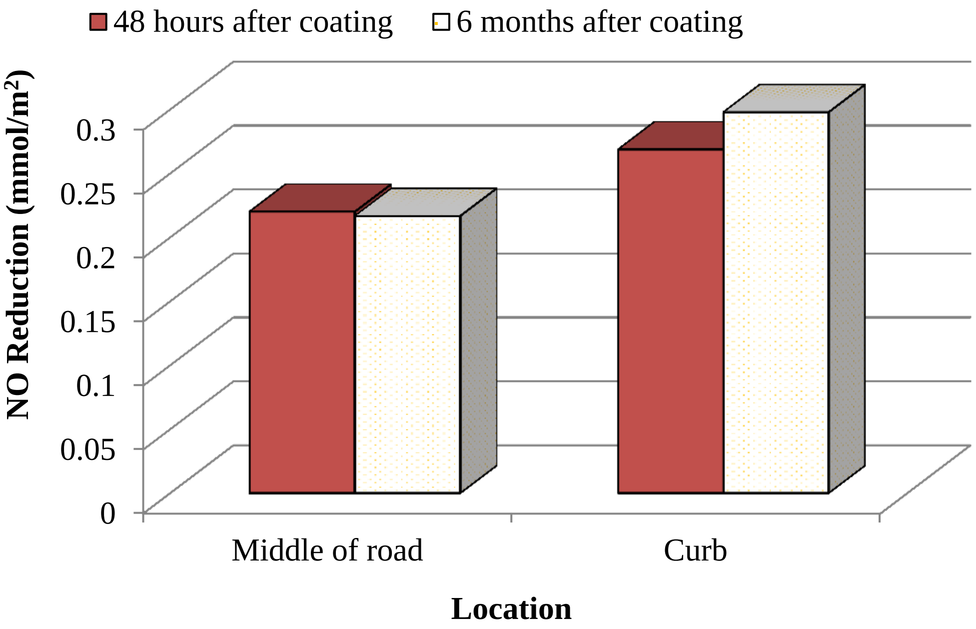


FIGURE 22: Comparison of NO reduction 48 hours after Application and Six Months after Application

5.3.2 Comparison of Field and Laboratory NO Removal Efficiency

Figure 23 compares the NO removal efficiency determined in the field one day after accumulation to the NO removal efficiency determined at different levels of relative humidity in the laboratory. The average relative humidity in the field during the collection period was 80%. As shown in this figure, there was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation and in the laboratory experiment at the same level of relative humidity. Results in Figure 23 also show that humidity had a negative impact on NO_x reduction efficiency in the laboratory as the increase in relative humidity resulted in a decrease in NO_x removal efficiency. It is possible that at high relative humidity, the water molecules interfere with NO_x contact to the TiO_2 active sites on the surface. However, past research by the authors showed that at relative humidity lower than 25% humidity, the lack of water molecules required for the hydroxyl radicals hinders the photocatalytic oxidation (22).

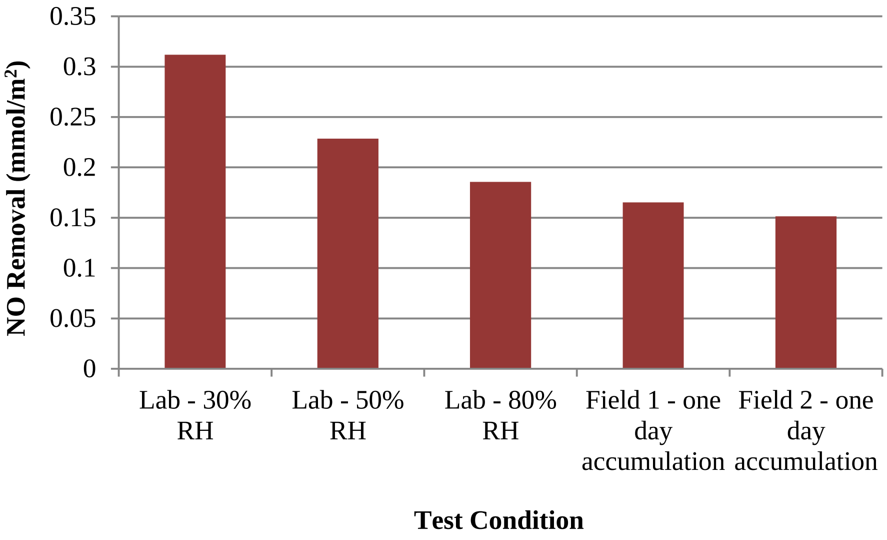


FIGURE 23: Comparison of NO Removal Efficiency in the Field and in the Laboratory

6.0 Summary and Conclusions

The US faces a significant challenge in controlling air pollution resulting from transportation activities and the growing population density. Validation of the effectiveness of photocatalytic pavements and their implementation in a manner that does not degrade the environment has the potential to expand use of this sustainable technology to mitigate many of the problems associated with pollution from motor vehicles. Hassan and co-workers laid the country's first air-purifying asphalt and concrete photocatalytic pavements on Dec. 20, 2010. The test area is a pavement site located on LSU campus. Based on the results of the experimental program, the following conclusions may be drawn:

- Results of the direct method and indirect methods of measuring photocatalytic degradation of NO_x show that there is evidence of a photocatalytic reaction occurring in the field. The photocatalytic process is very active during the first four days followed by a slight decrease in degradation rate of NO_x. Full regeneration of photocatalytic activity takes place in the field through a self-cleaning process during rain event.
- Six months of traffic and in-service operating conditions did not affect the efficiency of the photocatalytic coating as compared to its efficiency just after installation.
- There was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation and in the laboratory experiment at the same level of relative humidity.
- Environmental factors impacting photocatalytic efficiency are relative humidity, wind speed and direction, light intensity, and solar radiation. However, due to the variability

demonstrated in the results, additional factors such as vehicle activity and vehicle classification need to be considered.

7.0 Recommendations

Based on the results presented in this study, further research is recommended to validate the long-term efficiency of the technology, the influence of environmental parameters such as solar radiation and temperature on NO removal efficiency, and to determine the influence of TiO_2 application rate on photocatalytic efficiency in the field.

8.0 Outcomes

This work resulted in four journal papers:

1. Dylla, H., Hassan, M. M., and Osborn D., (2012). “Field Evaluation of Photocatalytic Concrete Pavements’ Ability to Remove Nitrogen Oxides.” Paper #12-2049, Journal of the Transportation Research Record, National Research Council, Washington, D.C., accepted for publication and presentation.
2. Asadi, S., Hassan, M. M., Dylla, H., Mohammad L., (2012). “Evaluation of Field Performance of Photocatalytic Asphalt Pavement in Ambient Air Purification.” Paper #12-2028, Journal of the Transportation Research Record, National Research Council, Washington, D.C., accepted for publication and presentation.
3. Osborn, D., Hassan, M. M., Dylla, H., (2012). “Quantification of NOX reduction via Nitrate Accumulation on a TiO2 Photocatalytic Concrete Pavement.” Paper #12-1832, Journal of the Transportation Research Record, National Research Council, Washington, D.C., accepted for publication and presentation.
4. Hassan, M. M., Mohammad L., Dylla, H., Asadi, S., and Cooper, S., (2011). “Laboratory and Field Evaluation of Sustainable Photocatalytic Asphalt Pavements” AAPT, under review.

In addition, an NSF CAREER proposal was submitted based on the results of this work. It is currently under review.

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