

Approximation Assessment of Photocatalytic Air Cleaning Pavements

James E. Alleman, Joel K. Sikkema, Peter C. Taylor

Abstract

This paper examines an approximation method to qualitatively assess the air-cleaning performance (i.e., specifically the elimination of aerial nitrogen oxide, NO, released within vehicular exhaust) by full-scale pavements which contain photo-catalytically reactive titanium dioxide under optimal conditions. Two hypothetical road configurations were considered using this method, including both a two-lane, low traffic density (i.e., 4,000 full-day AADT) and a four-lane, moderate traffic density (i.e., 10,000 full-day AADT) design. These options were then comparatively examined on the basis of expected European Union or United States vehicular emission levels. In each case, this method's day-time-only percentile elimination approximation results were derived using an extrapolation of lab-based specific contaminant elimination rates (i.e., mass NO removed per surface area per time) relative to contaminant release rates which were projected for EU or US vehicular contaminant emission levels. Using this paper's approximation method, and assuming best-case scenario conditions (i.e., original, un-aged, peak catalytic performance under optimal temperature, relative humidity, etc. conditions), day-time-only percentile removals in the ~mid-60% to ~90% range were predicted for EU two- and four-lane roadways with low to moderate traffic densities. These EU contaminant elimination approximation percentiles were higher than the actual, observed range (e.g., typically ~mid-10% to ~mid-60% day-time removal percentiles) of published contaminant elimination values which had been measured according to gas-phase contaminant changes during a number of full-scale studies completed at various EU locations and with EU-related vehicle types and emissions. In the case of similar US highway options, this method's approximated day-time-only elimination percentile results were lower than what was predicted for similar EU road options, with a range of ~30% to ~40%. These latter, lower US road approximations were believed to be related to higher expected US versus EU vehicle emission levels (i.e., by a factor of ~two- to ~three-fold for light and heavy duty vehicles).

Introduction

International interest has continued to grow in regards to the potential air-cleaning capabilities and full-scale application of photocatalytic concrete pavement (i.e., and other highway-adjacent structures, including crash barriers, noise walls, etc.) and building surfaces which contain titanium dioxide. Indeed, this interest is prompted by the expected beneficial capability of these photocatalytic surfaces when suitably exposed to solar ultraviolet irradiation to help remove otherwise reactive and problematic contaminants (e.g., such as inorganic nitrogen oxides or organic volatile compounds). Given this interest, therefore, the body of knowledge regarding these photocatalytic pavements continues to expand on both fundamental and pragmatic levels facilitated by an ongoing combination of academic, public, and private sector evaluation (i.e., as cited within the following 'General Overview' section of this paper).

Based on the latter interest, considerable past and ongoing experimentation has accordingly been applied to evaluating the efficacy of these photocatalytic surfaces. As will be covered in more detail within upcoming sections of this paper, these studies have included both lab- and full-scale experimentation where researchers examined a range of factors believed to be linked with observed performance. Within the lab-level testing efforts, these evaluations have typically examined a group of environmental factors, notably including ambient relative humidity, air temperature, solar insolation intensity (and specifically ultraviolet irradiation), aerial contaminant concentration, and duration of reactive contact. The approach used for surface-finishing newly constructed surfaces has also been evaluated (and considered to be another a potentially important variable; Hanson [2013]). Taken collectively, therefore, this published, lab-based knowledge about the general performance and specific rate characteristics of photocatalytic pavement reactivity has considerable intrinsic value as a foundational starting point with developing predictive, albeit approximate and best-case scenario, estimates with performance which might possibly be achieved at full-scale sites.

When considering the performance studies published for full-scale assessments, the vast majority of these studies were more-so focused on directly measuring net percentile levels based on observed aerial contaminant removal (see Table 1). Admittedly, a limited number of these full-scale studies also involved on-site analyses of actual surficial elimination rates, using a field-based surface gas-contact measurement plate device intended to mimic lab-based surface testing. This latter evaluation strategy, though, is not normally used, and as such quantified on-site surficial elimination rates are not routinely determined such that these rates could then be extrapolated to other pavements.

The concept of characterizing percentile-based contaminant elimination based on observed gas-phase removal is understandable given that several important performance factors (i.e., temperature, relative humidity, UV irradiance, etc.) are inherently subject to daily, seasonal, etc. *in-situ* fluctuations under real-world, full-scale conditions. However, whether or not full-scale observations of percentile contaminant removal can be used to predict contaminant elimination performance at other sites is subject to question. Notably, will the performance (and percentile contaminant removal level) observed with pavement ‘X’ be similarly observed at pavement ‘Y’ when these ‘X’ and ‘Y’ pavements have different physical dimensions and have varying levels of reactive surface area? Similarly, how will these varied pavements behave when they involve different vehicular traffic densities, different types of vehicles with varied exhaust emission levels (e.g., larger, heavier, higher polluting US engines *versus* typically smaller, lighter, cleaner EU engines), etc.? And yet another important variable would be the issue and extent of possibly evolving air-cleaning performance in relation to pavement aging and associated changes in photocatalytic reactivity.

This paper consequently explores an alternative conceptual strategy for approximating photocatalytic air contaminant elimination on a full-scale estimation basis. This method’s approach, though, has an important qualification where it makes several key assumptions on what are likely to be a best-case scenario. For example, this paper’s approximation method not only assumes optimal environmental conditions but also uses a presumed peak rate of photocatalytic reactivity which was extrapolated from lab-scale testing completed with fresh, un-aged, best-possible photocatalytic catalytic specimens. The suitability of this new approach for

qualitatively approximating TiO₂ pavement performance based on specific surficial reactivity, though, can also be drawn from recent efforts to evaluate similarly photocatalytic building, roofing, cladding, etc. surfaces, where much the same transition from only evaluating gas-phase percentile-removal performance to considering specific surficial elimination rates has also taken place.

As mentioned previously, and explained within the following section of this paper, this method involves multiple assumptions covering a set of elimination rate and environmental factors. Only one such environmental factor was taken into account, however, with each example used to demonstrate this model's outcomes (i.e., that of the impact with ambient NO contaminant levels in the ~50 part per billion by volume [i.e., ppbv] range *versus* a 1,000 ppbv level typically used for calibrating maximal lab-scale surficial reactivity). This assumed ambient concentration was chosen for two reasons. First, this level matches up with the 53 ppbv regulatory level established by the USEPA (2015) national ambient air quality standard for nitrogen dioxide (NO₂), where NO is the critical precursor species for this regulated nitrogen dioxide parameter. Second, this level also matches up with actual ambient US air contaminant levels, as were identified within a recent USEPA (2014) web-based posting for 'National Trends in Nitrogen Dioxide Levels' extending until 2014. After making this assumption, therefore, an ambient NO concentration of ~50 ppbv would subsequently reduce the predicted peak specific elimination rate by nearly a ~three-fold level.

There are also additional, multiple factors where even lower contaminant elimination rates might be experienced. Indeed, these sorts of less reactive pavements could occur with non-optimal temperature, relative humidity, reduced solar and UV irradiation, dirt-, grime-, and oil-blinding of the reactive surface, etc. In turn, each (or even all) of these potentially retarding impacts would warrant further consideration for those more carefully considered performance predictions where these sub-optimal circumstances would be expected.

The paper's approximation method subsequently assumed the following six factors: 1) an initial lab-derived contaminant elimination rate considered to be a best-case value (i.e., ~50 nmol NO·m⁻²·s⁻¹, under optimal conditions), 2) an approximately ~three-fold reduction in the actual specific contaminant elimination rate (i.e., down to ~20 nmol NO·m⁻²·s⁻¹) based on an expected ambient contaminant concentration (i.e., ~50 ppbv NO versus ~1000 ppbv NO typically used within lab-scale reaction rate studies), 3) pavement dimensions (i.e., net surface area, including both lane and shoulder areas paved with the photocatalytic materials), 4) daily traffic density during day-time, solar-irradiated periods, 5) distribution of vehicular types, whether light- or heavy-duty engine levels, and 6) expected cumulative contaminant emission rates for a projected light- plus heavy-duty vehicle makeup and emission levels relative to either EU or US norms.

The following key observations can subsequently be drawn from the following approximation examples outlined within this paper:

- 1) Photocatalytic pavements appear likely to perform better (i.e., with higher NO elimination levels) within full-scale EU applications than full-scale USA sites due to the expected lower contaminant emission levels which might be expected with EU vehicles (i.e., such that they impose a lower contaminant burden on photocatalytic pavements).

- 2) An EU two-lane, low-traffic density (i.e., estimated at 4,000 total AADT, and having 3,000 ‘day-time-only’ vehicles during sunlight irradiation) road would appear to have a projected peak (i.e., assumed peak ~summer-time reactivity) photocatalytic NO elimination rate which matched (or even slightly exceeded that of the involved vehicular exhaust rate (i.e., such that ~100% NO removal might be achievable under the assumed, best-case scenario conditions).
- 3) This latter predicted EU performance estimate decreased when considering a four-lane, higher traffic density highway (i.e., estimated at 10,000 AADT, and having 7,500 ‘day-time’ vehicles during sunlight irradiation), to a ~70% elimination level.
- 4) These approximated EU removal percentiles, at ~100 and ~70% elimination levels, are higher than the removal percentiles previously documented at multiple European highway locations (i.e., where these published values ranged between ~mid-10% to approximately 60% values). This decreased range may reflect that fact that the documented full-scale tests were completed on older, aged pavement sections under less-than-optimal real-world environmental conditions, where maximal photocatalytic performance (i.e., with fresh, un-aged pavement) would likely have been decreased.
- 5) The higher contaminant emission levels expected with inherently larger, heavier, higher polluting US vehicles appears to present a larger challenge for photocatalytic elimination, with commensurately lower expected removals.
- 6) A US two-lane, 4,000 AADT (i.e., 3,000 ‘day-time’ traffic density) highway was predicted to have an approximate summertime (i.e., again, assuming peak reactivity based on all environmental factors with the exception of the aerial contaminant level) photocatalytic NO elimination percentile at a ~40% level at the predicted US vehicular exhaust rate. This elimination performance was even lower with a modelled four-lane, higher AADT highway, at a ~30% level.
- 7) Again, these approximations with contaminant elimination would likely decrease in relation to daily or seasonal weather variations as the photocatalytic efficiency of these pavement surfaces declined under non-optimal environmental conditions (i.e., relative to temperature, relative humidity, solar insolation plus UV irradiance intensity, etc.). Even then, the original, optimal photocatalytic activity assumed for these roadway surfaces with this qualitative approximation method might also decline in relation with progressive age-related surface blinding, dirt or grime buildup, etc. None of these impacts, though, were factored into the approximations presented within this paper, and as mentioned previously these predicted results should clearly be characterized as best-case scenario outcomes. Considering this paper’s approximation results with an EU low-traffic density roadway, for example, the difference between approximation model prediction (~100%) and observed (i.e., ~15 to ~60%) elimination percentiles might conceivably reflect this very sort of un-aged, optimal *versus* aged, reduced-active surficial activity.

General Overview of Full-Scale Photocatalytic Performance Factors

Before exploring this new estimation method and associated results, the following synopsis addresses the various factors which may impact the air-cleaning capabilities of a photocatalytic pavement. In each case, a short explanation is provided as to the rationale for the cause-and-effect correlations tied to these factors, plus an additional explanation as to how this factor was, or was not, considered within this paper’s predictive performance estimation method.

Variations in Solar Insolation and UV Irradiance: As their name implies, photocatalytic reactions need light, and more specifically ultraviolet (UV) light within the so-called UV-A spectrum. This UV fraction of sunlight's energy spectrum provides the photonic motivation to oxidatively convert water (hence the additional significance of relative humidity as a source of this water) into a set of highly reactive 'hydroxyl radical' ($^{\bullet}\text{OH}$) and 'superoxide radical-anion' ($\text{O}_2^{\bullet-}$) species (i.e., Sikkema, 2013; Ramirez, *et al.*, 2010) which are the actual catalytic agent for contaminant transformation and final elimination. UV-A irradiance intensities at or above about 5 to 10 $\text{W}\cdot\text{m}^{-2}$ intensity are typically considered a reasonable threshold to effectively drive the air-cleaning, contaminant elimination reactions. By comparison, Grant and Slusser (2005) have reported a mean daytime UV-A irradiance range within the United States between a far-northern $\sim 10 \text{ W}\cdot\text{m}^{-2}$ (Fairbanks, Alaska) to a far-southern $\sim 20 \text{ W}\cdot\text{m}^{-2}$ (Homestead, Florida). Solar insolation does follow a diurnal cycle, though, ramping up and down on a daily basis, and there would also be winter-time drops in these mid-day values by a factor of about 2 to 2.5. As such, the activating ultraviolet portion of the incoming solar energy should reach and/or exceed an optimal level for most of the sunlight day. And as a result, the expected reactivity of a photocatalytic surface would reach a peak within about an hour after sun-up and remain strong throughout the day ramping down until about the last hour prior to sun-set. While this variability in irradiation intensity has non-trivial significance, our estimation model assumed that this parameter was sufficiently high in value throughout the day to avoid any negative impact.

Variations in Constitutive TiO_2 Levels and Reactivity: The amount and type (i.e., highly reactive anatase- TiO_2 versus low-reactive rutile- TiO_2) of catalyst originally added to, or alternatively sprayed onto, a photocatalytic surface are important factors within the context of a pavement's full-scale air-cleaning performance. While these parameters are solely controlled by industry vendors and generally retained as a non-disclosed parameter, it is likely that material-specific variations with these factors account for the different 'reactivities' which have been observed by various researchers with both lab- and full-scale materials. Without this sort of further insight, though, our estimation modelling was conducted with an assumed best-case elimination rate drawn from a group of similar lab-based observations. These assumptions could be refined in the event that vendors decide to either provide exact percentile composition data for their cement mixtures, or should they provide either elimination percentile or surficial reactivity rate guarantees for their product's achievable elimination performance and rates.

Variations in Environmental Relative Humidity (RH): As mentioned above, surficial water is required for these photocatalytic reactions, where this moisture again serves as the precursor for the formation of catalytic hydroxyl radicals. This water, however, is both a blessing and curse for photocatalytic surfaces. While some amount of water is needed, and even consumed during the photocatalytic reactions, too much water will start to degrade a surface's catalytic reactivity due to blinding of the necessary UV irradiation. Indeed, and as noted by a variety of researchers (e.g., Sikkema, 2013; Hüsken, *et al.*, 2009; Demeestere, *et al.*, 2009; Murata, *et al.*, 2000; Murata and Tobinai, 2002), higher relative humidity values actually provided successively lower elimination rate percentile. Demeestere, *et al.*'s (2009) observations showed that successive increases of RH to 1, 30, 52, and 77% levels generated successive reductions in percentile contaminant

elimination to 78, 65, 47, and 16% removals. Similarly, a ~50% reduction in the lab-scale contaminant elimination rates have been observed at ~50% RH levels (i.e., Murata, et al., 2000 and Sikkema, 2012). Here again, this relative humidity factor was similarly ignored within our preliminary estimation model, but could be considered within any further refinement of a performance prediction.

Variations in Environmental Temperature: Catalytic chemical reactions of all sorts, including those of a photocatalytic nature, tend to exhibit an inverse rate relationship with temperature. As temperature declines, catalytic reactions tend to slow down. Observations by various photocatalytic pavement researchers (i.e., Beeldens, *et al.*, 2011, Dylla, *et al.*, 2011, Chen and Chu, 2011, Herrmann, 1999, and Sikkema, 2013) have all examined this issue. Admittedly, there have been vague and even contrary findings in the case of some research findings with the impact of temperature, but the general convention would be that warmer pavements have higher contaminant elimination rates and colder pavements do not. Once again, this temperature factor was ignored within our preliminary estimation model, on the basis of estimating elimination rates where temperature was sufficiently high to not retard reactivity.

Seasonal Variations in Vehicular Exhaust Contaminants: Air temperature will also impact the fuel conversion efficiency, and exhaust gas strength, with internal combustion engines used in vehicles. In turn, there is a compounding effect during cold weather periods, where cooler air and pavement surface temperatures will reduce the contaminant elimination rate at the same point as the colder weather also causes a higher release of vehicular contaminants. As such, the overlapping impact of higher-contaminants and lower-elimination will yield less effective cold weather air-cleaning performance. For the purposes of the estimation efforts reported within this paper, though, this factor is irrelevant.

Variations in Aerial Contaminant Concentrations: Based on the findings presented by a number of published bench-scale studies (i.e., Sikkema, 2013; Murata, *et al.*, 2000; Hüsken and Brouwers, 2008; Husken, *et al.*, 2009; Ballari *et al.*, 2010; Ballari *et al.*, 2011), there is positive correlation between the concentration of a contaminant gas (e.g., NO) and the rate at which this contaminant might be catalytically eliminated. The significance of this relationship is understandable, in that having more contaminant present within a pavement's overlying gas volume would then set up a concentration gradient (i.e., bulk gas phase contaminant level less assumed near-zero contaminant level at the reactive surface) which accelerated this gas's transport and movement towards, contact with, attachment to, and catalytic conversion by the underlying reactive surface.

Variations in Roadway Configuration, Layout, Shading, and Aerial Dilution: The location, topographic openness, surrounding building layout, wind speed, and perhaps even compass orientation of a photocatalytic pavement can also be expected to impact the rates of both aerial contaminant dilution and elimination. For example, so-called street-canyon sites within inner-urban locations might be expected to experience less wind-induced dilution and higher contaminant buildup, which might then favor higher photocatalytic removal...as long as the necessary solar irradiation remains unblocked and/or unshaded. Several of the published full-scale studies showing higher-level (i.e., ~60% level) contaminant elimination percentiles were

completed under these sorts of conditions (see Table 1). On the other hand, though, far more open highway settings accompanied by higher ambient winds would likely experience much greater levels of wind-induced dilution, such that the contaminant ‘removal’ might then be attributed (perhaps to some extent mistakenly) to lateral wind-induced drift and aerial dilution versus actual reactive elimination. The assumption regarding wind and wind-borne dilution, drift, etc. with this method, though, was that there was no such prevailing wind.

Lab-Based Elimination Rates for NO: The published results for best-case lab-based measurements of contaminant elimination rates observed with varying gas contaminant concentrations, test cell gas flow rates (i.e., and resultant test contact times), ambient temperatures, ambient relative humidity, and varied solar insolation, tend to fall at or below a peak value (i.e., when exposed to 1,000 ppbv NO) of about ~30 to ~60 nanomoles NO eliminated per square meter of pavement surface area per second [i.e., $\text{nmol NO} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$] (Murata, et al., 2000; Murata and Tobinai, 2002; Sikkema, 2013; Overman, 2009; Hüsken, et al., 2009; Ballari *et al.*, 2010a; Ballari *et al.*, 2011). In one instance (i.e., Murata, et al., 2000; Murata and Tobinai, 2002), these authors reported peak specific elimination rates several times higher (i.e., from ~200 to ~300 $\text{nmol NO} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), but multiple other studies have shown peak, optimal rates in fairly close proximity to a lower peak value of about ~50 $\text{nmol NO} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ level. Furthermore, the predictive model developed by Ballari *et al.*, 2010b to calculate rates of NO elimination (rNO) on the basis of ambient contaminant levels produced a similar peak value of ~50 at a 1,000 ppbv NO level. Here again, the fact that different researchers have reported somewhat varying peak elimination rates likely reflects inherent variations in material properties (i.e., percent TiO_2 , anatase versus rutile fraction, etc.) which are rarely, if ever, known to or characterized by the involved researchers.

Elimination Rates for Other Air Contaminants: With a goal of further validating the latter NO elimination rate values, it is worth comparing these latter NO-related rates against those observed for other air contaminants subject to photocatalytic elimination. For example, this comparison can be derived using literature results observed with the removal of volatile organic compounds (i.e., VOC’s such as benzene, toluene, ethylbenzene and xylene, otherwise known as BTEX) where these compounds are found within vehicle fuels and would also represent important highway contaminants. After adjusting the published BTEX-type contaminant elimination rates to the same sort of $\text{nmol NO} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ units cited previously for NO elimination, the following observed rates have been reported for either BTEX or specific toluene removal:

- 56 $\text{nmol BTEX} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$; Strini, Cassese, and Schiavi (2005)
- 145 $\text{nmol toluene} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$; Ramirez, *et al.* (2010)
- 300 $\text{nmol toluene} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$; Demeestere, *et al.*, (2009)

This sort of direct comparison with contaminant elimination rates likely warrants further adjustment on the basis of photocatalytic electron flow required to sustain a specific elimination rate, where the oxidation of nitrogen oxide (i.e., three electrons required per mole of oxidized NO) needs far fewer electrons (i.e., twelve times less) than is required for oxidatively eliminating a far more reduced organic compound such as toluene (i.e., requiring thirty-six electrons per mole of toluene). Taking this difference into account, relative to electron flow rates seemingly

able to be achieved with BTEX organics, it would appear that an assumed peak NO elimination rate of $\sim 50 \text{ nmol NO} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ is reasonable, and perhaps even lower than would have been expected.

Comparative Full-Scale Percentile Removal Observations

The following overview provides a sampling of published full-scale roadway test results for photocatalytic systems. This information offers a comparative framework for considering the alternative approach of qualifying prospective contaminant elimination on the basis of extrapolated specific elimination rates relative to assumed pavement dimensions, traffic densities and makeup, and projected vehicular contaminant release rates.

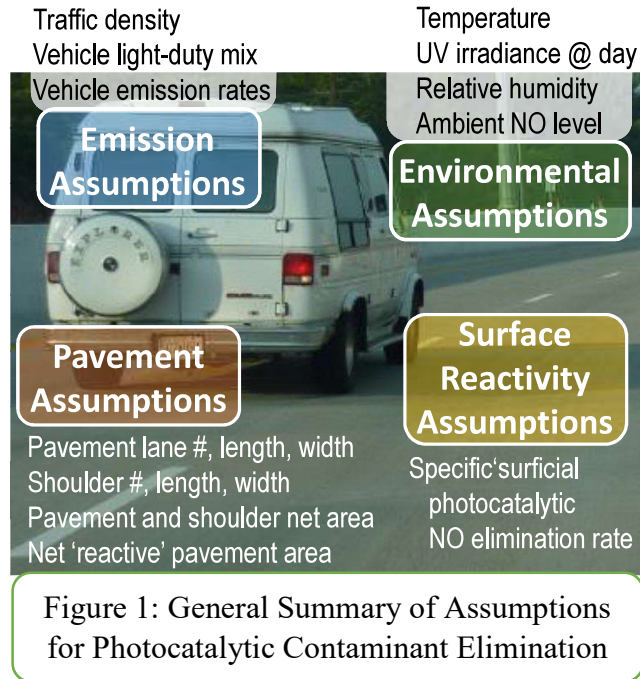
Year	Author(s)	Testing Conditions and Performance Observations	Observed Percentile NO Removal Levels
2006	Plassais and Guillot (Note: cited by Guerrini and Peccati @ 2007)	Location: Via Morandi, Segrate, Italy Surface: Thin mortar overlay	60% max
2007	Guerrini and Peccati	Location: Borgo Palazzo, Bergamo, Italy Surface: Concrete paving blocks	66% max 20% min
2007 2009	Guerrini and Peccati Borgarello	Location: <u>Rue Jean Bleuzen, Vanves, France</u> Surface: Concrete overlay	20% min
2009	Borgarello	Location: Calusco d'Adda, Bergamo, Italy Surface: Concrete block	45% avg
2009	Borgarello	Location: <u>Porpora Street, Milan, Italy</u> Surface: Concrete, photo-catalytic ceiling paint	23% @ minimum UV irradiance level
2009	Rousseau	Location: St-Denis, France Surface: Concrete overlay	30% @ 2 m height 15% @ 20 m height
2009	Overman	Location: Hengelo-Overijssel, The Netherlands Surface: Paving stones w/ TiO ₂ concrete topping	2-10% @ late winter day
2010	Gignoux, <i>et al.</i>	Location: Vanves, France Surface: Concrete paving blocks	40-50% avg
2013	Ballari and Brouwers	Location: Hengelo, The Netherlands Surface: Concrete paving blocks	19% avg

Two noteworthy aspects can be drawn from this tabular summary:

- 1) These testing locations were all within the EU, where the expected vehicular exhaust levels would be expected at lower vehicular contaminant release rates than would be expected within the US.
- 2) Many of these observed full-scale NO removal percentiles are notably high, with several in excess of 40% and reaching ~60%.

Basic Assumptions Applied to New Performance Estimation Method

The adjacent Figure 1 summary lists the basic environmental, pavement, emission, and specific elimination rate assumption categories which were considered in the four estimations (i.e., EU two- and four-lane road, and US two- and four-lane road) reported on within this paper. In each case, these assumption categories involved a further sub-set of further assumptions which were cumulatively considered within each final estimation assessment. Further detailed breakdowns of these sub-set assumption factors and their associated settings are provided in the following summary. In this regard, though, there are ultimately three major primary factors being considered: 1) the predicted surficial reactivity rate for contaminant elimination, 2) the net, photocatalytic surficial area of the pavement, and 3) the cumulative contaminant emission load released at this pavement site.



Environmental Assumptions:

Seasonal option	Summer (assumed optimal season due to temperatures and expected higher solar insolation magnitude and duration)
Day versus night	Daytime, sun-illuminated
Solar insolation level	Assumed full-sun, non-cloudy solar insolation with non-limiting UV irradiance levels (<i>i.e.</i> , $\geq 10 \text{ W/m}^2$)
Air temperature	Assumed non-limiting summer warm/hot temperature ($\sim > 85^\circ\text{F}$)
Relative humidity	Assumed non-limiting relative humidity levels @ low to moderate values (<i>e.g.</i> , $\sim > 5\text{-}10\% \text{ RH}$)
Wind-induced aerial dilution and/or lateral drift	Assumed to be nil (<i>Note: this is an admittedly unlikely circumstance, but this assumption was adopted for the sake of simplicity; conversely, though, wind-induced dilution and/or migration either vertically or laterally of emission contaminants away from photocatalytic contact with the pavement would be expected to occur.</i>)
Ambient contaminant (NO)	$\sim 50 \text{ ppbv}$

concentration level	<i>(Note: this assumption impacts the assumed specific elimination rate; the justification stems from an assumed ambient NO being approximately equivalent to that of the USEPA National Ambient Air Quality Standard (NAAQS) for secondary annual average nitrogen oxides concentration @ 53 ppbv (i.e., which are inherently based on vegetation damage)</i>
---------------------	--

Pavement Assumptions:

Traffic lanes	Either two- or four-lane pavement designs
Traffic lane dimension	12ft lane width
Shoulder presence	Yes; similarly paved with photocatalytic pavement
Shoulder dimension	4ft shoulder width (on two sides)
Net photocatalytic pavement surface area on a cumulative per-mile basis	Two-lane plus shoulders = 15,697 square meters Four-lane plus shoulders = 27,469 square meters

Vehicle Emission Assumptions:

Traffic average daily density	Two-lane system = 4,000 vehicles per 24-hr day and night period Four-lane system = 10,000 vehicles per 24-hr day and night period
Traffic 'day-time-only' density (assumed $\frac{3}{4}$ traffic flow @ day and $\frac{1}{4}$ @ night)	Two-lane system = 3,000 vehicles per ~12-hr 'day-time-only' period Four-lane system = 7,500 vehicles per ~12-hr 'day-time-only' period
Vehicular type distribution	85% light-duty sedan and truck/gasoline; 15% heavy-duty/diesel <i>(Notes: This 85-15% breakdown for a light-heavy-duty vehicle composition was estimated on a qualitative basis relative to expected net vehicular NO emission percentiles reported by Kota, et al., 2014)</i>
Low-traffic density count @ ~12-hr day-time-only period	2,550 light-duty vehicles 450 heavy-duty vehicles
Moderate-traffic density count @ ~12-hr day-time-only period	6,375 light-duty vehicles 1,125 heavy-duty vehicles
EU vehicle emissions *	
EU Light-duty emissions	0.1 gm NO/mile (see EU emission justification below)
EU Heavy-duty emissions	0.3 gm NO /mile (see EU emission justification below)
US vehicle emissions *	
US Light-duty emissions	0.2 gm NO /mile (see US emission justification below)
US Heavy-duty emissions	1.06 gm NO /mile (see US emission justification below)

* Notes:

- (1) The preceding EU emission estimates were based on 'Wikipedia - European Emission Standards' (2012), and reflect so-called Euro-5 emission standards currently in effect;
- (2) The preceding US emission details were based on the California Emission Factor Tables (2013) and Moyer Guidelines (2011).

Surface Reactivity / Contaminant Elimination Rates:

Optimum, non-limiting specific contaminant elimination rate (Note: see following narrative explanation of this assumed optimal lab-based surficial reactivity rate)	$\sim 50 \text{ nmol NO} \cdot \text{m}^2 \cdot \text{s}^{-1}$
Actual specific contaminant elimination rate (Note: This activity reduction was assumed due to a limiting ambient NO concentration level of $\sim 50 \text{ ppbv}$)	$\sim 20 \text{ nmol NO} \cdot \text{m}^2 \cdot \text{s}^{-1}$

The latter assumption regarding the predicted NO contaminant elimination rate was based on a derivation of this estimated value using the model published by Ballari, *et al.*, 2010b, as depicted in the adjacent Figure 2 graphic. This non-linear modeling solution for the rate of NO elimination (i.e., r_{NO}) was developed as a function of the ambient NO concentration (i.e., CNO), where as previously mentioned this level was assumed to be equivalent to that of the USEPA NAAQS secondary air quality standard for nitrogen dioxide at 50 ppbv.

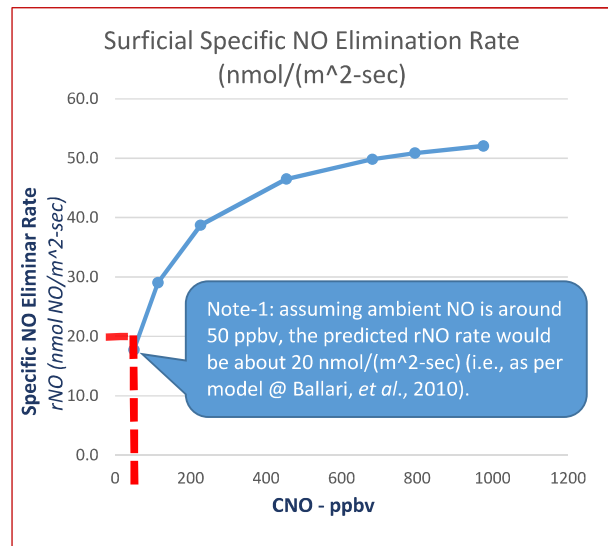


Figure 2: Modeled Prediction of Photocatalytic Contaminant Elimination Rate, r_{NO} [Reference: Ballari, *et al.*, 2010b)]

Exemplary Performance Estimation Results

Example Approximation #1 - EU Pavement @ Two-Lane, Low-Traffic Density Conditions:

- First, the following calculation approach was used to approximate the contaminant emission levels for the circumstance of this assumed two-lane, low traffic-density road's traffic mix:

$$(\# \text{ light-duty vehicles during day-time-only period}) \times (\text{EU light-duty vehicles NO emission rate per mile [gms/vehicle-mile]}) + (\# \text{ heavy-duty vehicles during day-time-only period}) \times (\text{EU heavy-duty vehicle NO emission rate [gms/vehicle-mile]})$$

This equation subsequently estimates a contaminant release mass of 390 gms NO per one-mile road length.

- Second, the following calculation approach was used to estimate the contaminant elimination capacity for the circumstance of this assumed road's surface area:

(Pavement surface area [m²]) x (Surficial photocatalytic NO elimination rate [i.e., adjusted from units of nmole/m²-sec to units of gms/m²-hour]) x (Day-time-only sunlight period [12 hrs])

Using the latter approximated ‘removal’ calculation, the calculated contaminant elimination rate for this road’s reactive surface area would be 407 gms NO eliminated per one-mile road length.

- Third, these approximation results, therefore, suggest that complete elimination of vehicular NO emissions would be reached under the assumed conditions (i.e., given that the ‘elimination’ value slightly exceeds the ‘emission’ value).
- Fourth, this approximation result is higher than the published values for full-scale EU photocatalytic pavement test sites.

Example Approximation #2 - EU Pavement @ Four-Lane, Moderate-Traffic Density Conditions:

- First, the similarly calculated contaminant emission levels for this assumed road’s traffic would equate to 975 gms NO released per one-mile road length.
- Second, the similarly calculated contaminant elimination capacity for this road’s larger reactive surface area would be 712 gms NO eliminated per one-mile road length.
- Third, these latter two values then correspond to an approximated 73% elimination percent.
- Here again, this approximation results is still higher than the published values for full-scale EU photocatalytic pavement test sites.

Example Approximation #3 - US Pavement @ Two-Lane, Low-Traffic Density Conditions:

- First, using the same approach as per the EU road calculations (albeit adjusted for US versus EU emission levels), the approximated contaminant emission levels for this assumed road’s traffic would equate to 987 gms NO released per one-mile road length. This value is higher than calculated for an EU road system (with similar traffic density plus makeup) given that the increase reflects the higher expected emission levels for US vehicles.
- Second, the calculated contaminant elimination rate for this road’s reactive surface area would still be the same 407 gms NO eliminated per one-mile road length as had been calculated with the similarly constructed two-lane (plus shoulders) EU road.
- Third, these values would then equate to a lower (~41%) elimination percent than that of the EU roadway.
- Fourth, this approximation is rather lower than the elimination levels which were reported for, let alone predicted for, the full-scale EU photocatalytic pavement test sites.

Example Approximation #4 - US Pavement @ Four-Lane, Moderate-Traffic Density Conditions:

- First, the similarly approximated contaminant emission levels for this assumed road’s traffic would equate to 2,468 gms NO released per one-mile road length, which again is higher than calculated for an EU road system with similar traffic density plus makeup (i.e., again due to the higher US vehicle emission levels).

- Second, the calculated contaminant elimination rate for this road's reactive surface area would still be the same 712 gms NO eliminated per one-mile road length as had been calculated with the similarly constructed two-lane (plus shoulders) EU road.
- Third, here again this removal would then equate to a lower (~29%) elimination percent.
- Fourth, this results is lower than what had been predicted for the similarly sized full-scale four-lane, moderate traffic-density EU photocatalytic road option.

Summary and Discussion

This paper's approximation strategy for evaluating the performance of photocatalytic pavements generated predicted removal percentiles for NO_x air cleaning which were higher than the published body of literature in terms of observed full-scale photocatalytic pavement performance, at least in the case of European road systems. Indeed, the published EU photocatalytic pavement findings have generally identified air contaminant (i.e., nitrogen oxide) elimination levels on the order of ~mid-teens to ~sixty percentile removals. In contrast, the approximated removals for both two- and four-lane EU roadways were higher, even to the point of predicting complete removal.

Using this same predictive approximation model to evaluate similarly configured US roadways (i.e., two-lane, low-traffic and four-lane, moderate traffic roadways) leads to lower approximated performance outcomes relative to those of EU roads. Indeed, the approximated removal outcomes for US photocatalytic highways ranged from 15% (four-lane moderate-traffic density) highway) to 22% (two-lane low-traffic density highway). Here again, these estimation results undoubtedly stem from the predicted higher polluting performance of US vehicular engines at both light- and heavy-duty vehicle levels.

These approximated findings suggest that a beneficial impact with partial (and perhaps even full) elimination of aerial NO might be reached within these roadway systems, at least for those applications where their design and environmental conditions plus actual rates of surficial contaminant reactivity are able to match the best-case assumptions with which these approximations were derived. In both cases, with either the EU or US approximations, it should be acknowledged that these approximated elimination rates might decline under less optimal conditions. For example, it would be reasonable to assume that lower elimination percentiles might be realized during colder, wintertime periods, or during cloudy periods with lower solar and UV irradiation levels, or during high relative humidity periods, or with aged pavements where surface cleanliness has declined due to grime, oil, etc. accumulation, etc. which blinds and blocks incoming solar energy, etc. The extent to which a fresh pavement's best-case performance might subsequently be achieved and sustained over a prolonged multi-year period is presently not well documented. And whether a pavement which has lost some portion of this photocatalytic capacity due to contaminant blinding, aging, etc. can be rejuvenated using surface cleaning, etching, grinding, etc. methods is again an unknown. This paper's approximation approach admittedly did not attempt to model any such circumstance, either in regards to age-related, etc. reduced performance or remedial rejuvenation practices. Interested practitioners should consequently continue to track the upcoming literature for further published improvements regarding the body of knowledge for this innovative technology.

References

- Ballari, M. M. and Brouwers, H. J. H. (2013). “Full scale demonstration of air-purifying pavement.” *Journal of Hazardous Materials*, 254–255 (2013) 406–414
- Ballari, M. M., Hunger, M., Hüsken, G., and Brouwers, H. J. H. (2010a). NO photocatalytic degradation employing concrete pavement containing titanium dioxide. *Applied Catalysis B-Environmental*, 95(3-4), 245-254. doi: 10.1016/j.apcatb.2010.01.002
- Ballari, M. M., Hunger, M., Hüsken, G., and Brouwers, H. J. H. (2010b). Modelling and experimental study of the NO_x photocatalytic degradation employing concrete pavement with titanium dioxide. *Catalysis Today*, 151, 71-76.
- Ballari, M. M., Yu, Q. L., and Brouwers, H. J. H. (2011). Experimental study of the NO and NO₂ degradation by photocatalytically active concrete. *Catalysis Today*, 161(1), 175-180. doi: 10.1016/j.cattod.2010.09.028
- Beeldens, A., Cassar, L., and Murata, Y. (2011). Applications of TiO₂ Photocatalysis for Air Purification In Y. Ohama and D. Van Gemert (Eds.), *Application of titanium Dioxide Photocatalysis to Construction Materials* (1st ed.): Springer.
- Borgarello, E. (2009). “TX Active by Italcementi: The Photocatalytic Active Principle.” Technical Report, Italcementi, Italy, 39 pgs.
- California Emission Factor Tables (2013). “Methods to Find the Effectiveness of Funding Air Quality Projects.” California Air Resources Board, May 2013.
- Chen, M., and Chu, J. W. (2011). NO(x) photocatalytic degradation on active concrete road surface - from experiment to real-scale application. [Article]. *Journal of Cleaner Production*, 19(11), 1266-1272. doi: 10.1016/j.jclepro.2011.03.001
- Demeestere, K., Dewulf, J., De Witte, B., et al. (2008). “Heterogeneous photocatalytic removal of toluene from air on building materials enriched with TiO₂.” *Building and Environment*, 43, 4, pgs. 406-414.
- Dylla, H., Hassan, M. M., Schmitt, M., Rupnow, T., and Mohammad, L. N. (2011). Laboratory Investigation of the Effect of Mixed Nitrogen Dioxide and Nitrogen Oxide Gases on Titanium Dioxide Photocatalytic Efficiency in Concrete Pavements. *Journal of Materials in Civil Engineering*, 23(7), 1087-1093. doi: 10.1061/(asce)mt.1943-5533.0000248
- Gignoux, L., Christory, J-P., and Petit, J-F. (2010). “Concrete Roadways and Air Quality – Assessment of Trials in Vanves in the Heart of the Paris Region.” In Proceedings of the 12th International Symposium on Concrete Roads, Sevilla, Spain, 13–15 October 2010.

- Grant, R. H., and Slusser, J. R. (2005). Estimation of ultraviolet-A irradiance from measurements of 368-nm spectral irradiance. *Journal of Atmospheric and Oceanic Technology*, 22(12), 1853-1863. doi: 10.1175/jtech1823.1
- Guerrini, G.L. and Peccati, E. (2007). Photocatalytic Cementitious Roads for Depollution, International RILEM Symposium on Photocatalysis, Environment, and Construction Materials, 8-9 October 2007, Florence, Italy.
- Hanson, S. (2013). "Fabrication Techniques for Concrete Containing TiO₂ Photocatalytic Particles." 2013 International Concrete Sustainability Conference, San Francisco, California, 7 May 2013.
- Herrmann, J. M. (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today*, 53(1), 115-129.
- Hüsken, G. and Brouwers, H. J. H. (2008, June 16-20). *Air purification by cementitious materials: Evaluation of air purifying properties*. Paper presented at the International Conference on Construction and Building Technology, Kuala Lumpur, Malaysia.
- Hüsken, G., Hunger, M., and Brouwers, H. J. H. (2009). Experimental study of photocatalytic concrete products for air purification. *Building and Environment*, 44(12), 2463-2474. doi: DOI 10.1016/j.buildenv.2009.04.010
- Kota, S.H., Zhang, H., Chen, G., Schade, G.W., and Ying, Q. (2014). "Evaluation of on-road vehicle CO and NO National Emission Inventories Using an Urban-Scale Source-Oriented Air Quality Model." *Atmospheric Environment*, 85, 99-108.
- Moyer Guidelines (2011). "Carl Moyer Program Guidelines: Appendix D: Tables for Emission Reduction and Cost Effectiveness Calculations." California Environmental Protection Agency, Air Resources Board, Release Date: 6 June 2011.
- Murata, Y., Kamitani, K., and Takeuchi, K. (2000). Air Purifying Blocks Based on Photocatalysis. Paper presented at the Japan Interlocking Block Pavement Engineering Association World Congress 2000, Tokyo, Japan.
- Murata, Y., and Tobinai, K. (2002). Influence of various factors on NO removal performance of permeable interlocking block based on photocatalysis. *Journal of Structural and Construction Engineering (Transactions of AIJ)* (555), 9-15.
- Overman, H.T.J. (2009). "Simulation model for NO Distributions in a Street Canyon with Air Purifying Pavement." Unpublished MS Thesis, University of Twente, Enschede, the Netherlands, August 2009, 107 pgs.
- Plassais, A. and Guillot, L. (2006). "DePolluting Activity Assessment of Photocatalytic Cement-Based Materials: From Lab to Real-Scale Testing, 10th International Symposium on

Concrete Roads, Brussels, Belgium, 18-22 Sept 2006, 13 pgs (NOTE: referenced by Guerrini and Peccati, 2007).

- Ramirez, A.M., Demeestere, K., and De Belie, N., *et al.* (2010). "Titanium dioxide coated cementitious materials for air purifying purposes: Preparation, characterization and toluene removal potential." *Building and Environment*, 45, 4, pgs. 832-838.
- Rosseau, P., Drouadaine, I., and Maze, M. (2009). "Impact du procédé NOer sur la dispersion atmosphérique de NO issus du trafic routier." URL: <http://www.eurovia.com/media/2570938/article-NOer-2-rgra-mai-juin-2009.pdf>
- Sikkema, J.K. (2013). "Photocatalytic degradation of NO by concrete pavement containing TiO₂." Unpublished doctoral dissertation, Iowa State University, Department of Civil, Construction, and Environmental Engineering, Ames, IA.
- Strini, A., Cassese, S., and Schiavi, L. (2005). "Measurement of benzene, toluene, ethylbenzene and o-xylene gas phase photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor." *Applied Catalysis B-Environmental*, 61, 1-2, 90-97.
- USEPA (2014). National Trends in Nitrogen Dioxide Levels. URL: <http://www3.epa.gov/airtrends/nitrogen.html>
- USEPA (2015). National Ambient Air Quality Standards (NAAQS). URL: <http://www3.epa.gov/ttn/naaqs/criteria.html>
- Wikipedia - European Emission Standards. (2012). URL: https://en.wikipedia.org/wiki/European_emission_standards