environment innovation business

Towards Purer Air:

A review of the latest evidence of the effectiveness of photocatalytic materials and treatments in tackling local air pollution

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Foreword

Air pollution is one of the most challenging, and insidious, public health issues of our time. High urban concentrations of particulate matter and nitrogen oxides are estimated to be responsible for tens of thousands of premature deaths. The young and the old are especially vulnerable.

There is a wide agreement that air pollution must be reduced, but comprehensive solutions are elusive. Electric vehicles, for example, clearly have a role to play, but still create particulate matter through brake and tyre wear.

EIC represents the businesses which are working to solve environmental problems, including air pollution. Our member companies are innovative and include both technology manufacturers and expert consultancies. As an organisation we believe that there is no single solution to air pollution, but that a range of technologies and approaches will be needed, with an evidence-based assessment of the costs and strengths and weaknesses of each technology essential to decide what combination of measures will lower dangerous air pollution levels quickly and affordably.

This report is one of a number of reports we have published on the policies and technologies of air pollution. It focuses on the potential of photocatalytic treatments (PCT's) to reduce ambient levels of nitrogen oxides. If effective, such treatments could be applied to road surfaces and buildings in the most polluted urban streets. They would not be enough by themselves, but could be used as a relatively cheap and unobtrusive way to add to other efforts.

Studies have shown that photocatalytic treatments do work in laboratory conditions, something noted by the Government's Air Quality Expert Group. Can we ensure that this pollution reduction effect could be replicated at scale in the real world? AQEG thought not, pointing to a selection of field trials which had mixed results. Their report did recognise the value of further work, and given the need to leave no stone unturned in searching for solutions to air pollution, we decided to commission further research from Imperial College London to understand the implications of all available studies and trials in this field in as much depth as possible. We also commissioned EIC member consultancy Temple Group to undertake a new cost benefit analysis on the use of PCTs.

The conclusions of this research are set out in this report and give cause for optimism. We hope that the work will stimulate further debate over the value of conducting a number of large scale field trials to provide hard evidence of the role PCTs could play in cleaning up the polluted air we all breathe.

My thanks to Imperial College and to Temple Group for their detailed and thorough work.

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Executive Director
EIC

Introduction

This report contains an assessment of the most up-to-date evidence for the effectiveness of photocatalytic treatments (PCTs) on reducing nitrogen oxides. It summarises the results of two studies commissioned by the Environmental Industries Commission – the first by Imperial College London, which examined all the available published evidence from both laboratory studies and field trials, and develops a model of the likely impact of PCTs on a typical street canyon, and the second by environmental consultancy Temple Group, who has used the work by Imperial and additional analysis to calculate cost benefit analyses for a plausible scenario of PCT deployment. Both studies are included as Annexes to this report.

The report also includes recommendations from EIC for policymakers.

The need to tackle NO_X

Nitrogen oxides, and especially nitrogen dioxide, are harmful pollutants released when fossil fuels are burned. For public health reasons, the EU has set legal limits on NO_2 concentrations, which many UK towns and cities regularly exceed. The public health cost of these levels of NO_2 is estimated to be tens of thousands of premature deaths. There is a broad political and scientific consensus that levels of NO_2 in urban areas must be reduced as quickly as possible for public health reasons, and this is also a legal requirement under EU law.

There is currently an active debate over the policies and technologies that will reduce NO_2 levels in the most effective manner. Practicality, cost and speed of deployment are all key issues.

Most options being considered are either behaviour change options (reduced car use, switching off vehicle engines when stationary), or designed to cut out pollution at source (eg DPF/SCR exhaust treatments, low emissions fuels, or zero emission vehicles such as electric cars).

A further approach, complementary to the others, is to remove NO_x from the atmosphere in the most polluted areas. One way to do this is to apply photocatalytic treatments to surfaces in areas of high NO_x pollution.

Use of TiO_2

Titanium dioxide (TiO_2) is the naturally occurring oxide of titanium. It is used in a wide range of pigment related applications (e.g. as a white pigment in paint, a UV blocker in sunscreen, a food colorant etc). TiO_2 is also a powerful photocatalyst, and can speed up the natural, but slow oxidisation of organic matter in the presence of light and water.

Specialist photoactive TiO_2 is already used in a wide range of photocatalytic products, including self-cleaning windows (Pilkington NSG - Activ™, Saint-Gobain - Bioclean, PPG - Sunclean), self-cleaning tiles (TOTO - Hydrotect) and air purification devices (Hoover, electriQ, De'Longhi, Green UV etc). The current global market for photocatalytic compositions was $1.5 billion in 2014, and is forecast to grow at a compound annual growth rate of 12.6% over the next five years.

Photoactive TiO_2 is already being used in photocatalytic coatings for the abatement of NO_x in polluted air (Boysen Paints, Keimfarben, Sto Climisan, PPG and others). The core of this idea is to incorporate photoactive TiO_2 onto the surface of building materials, where under the action of UV light present in natural sunlight, ambient NO_x gases will be oxidised into benign compounds. Various products have been examined; including photocatalytic concretes, paints and asphalts. In addition to oxidising NO_x gases in air, these coatings can also oxidise sulphurous oxides, ammonia and VOCs into benign compounds (Guerrini, 2012).

Because of the global concern over air pollution in urban areas, there has been significant interest in the potential of photocatalytic treatments. Laboratory studies have been conducted as well as field trials in numerous places.

AQEG study

In 2016, the UK Government's Air Quality Expert Group produced a review of a number of these studies and trials [Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016]. The AQEG report recognised that 'Under laboratory conditions photocatalytic surfaces have been shown to effectively reduce concentrations of NO_x.'

The report then looked at a selection of field trials and concluded that they showed mixed results. AQEG then made a set of assumptions about the way that the airflow would interact with the PCT surface coating, and modelled the effectiveness of a PCT coating on reducing NO_x pollution in a typical London environment. The review concluded that the build up of NO_x in the London atmosphere would be six times greater than the removal capacity of the PCT coating, and that PCT treatments would have limited effect.

The AQEG report also pointed out that some studies had shown evidence of potential generation of harmful by-products during the photocatalytic reaction.

EIC-commissioned research

AQEG recognised that there are many uncertainties in assessing and modelling the effect of photocatalytic treatments, commenting that 'it is uncertain what magnitude of reduction in concentration might be expected under real conditions e.g. in urban streets due to the complex way in which the atmosphere interacts with surfaces.'

Given the theoretical potential of photocatalytic treatments to be a low cost, unobtrusive option to help tackle air pollution, EIC decided it was worth doing further analysis and in Autumn 2017 commissioned Imperial College London to undertake a thorough analysis of all available evidence including the most recently published. The full report from Imperial College is in Annex 1.

The Imperial College report examined both laboratory studies and field trials, for both photocatalytic concrete products, photocatalytic paints and treatments. The research was able to cover a much wider range of field trials than the AQEG report was able to (see table)

Table 1: Trials covered in AQEG and Imperial College reports

Trials covered by AQEG report	Trials covered by Imperial College report
Paris – 2004	Paris – 2004
	Antwerp – 2004
	Tower Hamlets – 2005
	Rome - 2007
Camden – 2007	Camden – 2007
Hengelo – 2008	Hengelo – 2008
	Manila – 2009
	Lousiana – 2011
	Wijnegem - 2011
Brussels – 2011	Brussels – 2011
Copenhagen - 2012	Copenhagen – 2012
	The Hague - 2013

Imperial College noted that in two large scale trials not covered in the AQEG report, Rome - 2007 (9,000 m^2 coating) and Manila (6,000 m^2 coating) 'showed significant decreases in NO_2 in the surrounding air'. Imperial College also noted that several of the trials considered by AQEG to be "not comprehensive and unreliable" did actually demonstrate viable reductions in pollution level.

The Imperial College research then modelled a scenario where photocatalytic paint and a road coating were used in a representative London street canyon (the urban architecture in which the impact of photocatalytic treatment would be most effective and where it would make sense to target any deployment of PCTs – they would not be appropriate for all urban areas). Pp 33-36 in Annex 1 set out the full details of the scenario and the modelling.

The conclusions are in the Table below, showing NO_x reductions of 4 to 11% and NO reductions of 11 to 28% depending on seasonal conditions.

Table 2: NO_x Reductions from photocatalytic treatment under different scenarios

Scenario	Season	Activity ($mg.m^{-2}.s^{-1}$)		NO_x reductions in moving volume of gas (2,400 m^3)	
		NO	NO_2	NO	NO_2
(i)	Summer	3.3	0.93	18.3 mg, 11.0%	5.2 mg, 4.4%
	Winter	5.9	1.12	32.8 mg, 11.1%	6.2 mg, 4.3%
(ii)	Summer	3.3	0.93	45.8 mg, 27.5%	12.9 mg, 11.0%
	Winter	5.9	1.12	81.8 mg, 27.7%	15.6 mg, 10.8%

These results are much higher than the AQEG modelling, which predicted NO_x reductions of only 0.7%. This difference is explained by:

- The Imperial College modelling used experimentally derived, published deposition velocities based on work by Engel and Bahnemann et al (2015). The values from Engel's study are an order of magnitude higher than the deposition values estimated in the AQEG modelling exercises. There is no experimental or technical justification for the AQEG estimate for deposition velocity of a photocatalytic surface in their report.

Modelling has inherent uncertainties, however it should be noted that the NO_x reduction rates in the Imperial College model were comparable to the reductions observed in the large scale Rome and Manila trials and other modelling studies which have been carried out.

Side products

A concern raised about the future deployment of PCTs is the formation of potentially harmful side products such as nitrous acid, (often referred to as HONO), and formaldehyde during reaction of NO_2 on TiO_2 paints. The AQEG report raised this risk. The Imperial College study notes that 'Some studies have shown that HONO levels increase (a harmful respiratory irritant) during the reaction of NO_2 on TiO_2-based paints (Gandolfo et al., 2015), whereas some studies show the contrary (Laufs et al., 2010).'

Work by Bahnemann et al. (2014) indicates that if a photocatalyst is powerful enough to degrade NO_x into intermediate forms, these forms are readily and rapidly converted fully to harmless nitrate by oxidation.

Cost-benefit analysis

Given the range of technology options available to tackle air pollution, it makes sense to prioritise those which have the best cost-benefit ratio. In 2015, EIC commissioned Temple Group to undertake a cost benefit analysis of five technologies, including PCTs, under certain scenarios. For this new report, EIC asked Temple Group to update the modelling for the PCT scenario using the analysis from the Imperial College work, and Temple Group's own updated analysis of the cost of applying and maintaining PCTs. Full details of Temple Group's methodology can be found in their report which forms Annex 2 of this report. The conclusions were that the NPV costs would be as follows:

Table 3 Net Present Value (NPV) cost of photocatalytic treatment per tonne of NO_x abated

Scenario	Data	Units
Low cost scenario to 2020	23,530	£/teNO_x
Mid cost scenario to 2020	40,523	£/teNO_x
High cost scenario to 2020	73,203	£/teNO_x
Low cost scenario to 2030	18,729	£/teNO_x
Mid cost scenario to 2030	32,255	£/teNO_x
High cost scenario to 2030	58,267	£/teNO_x

For comparison, the equivalent costs per tonne for an electric vehicle roll out scenario (as calculated in 2015) were in the order of £1m/tonne of NO_x abated.

Conclusion and recommendations

This report is intended to be an evidence-based contribution to the ongoing debate about technology options for tackling air pollution generally, and the potential role of PCTs specifically. Given the thoroughness of the Imperial College research, it seems that the AQEG conclusions were too pessimistic in their assessment of PCTs. Given the inherent uncertainties in modelling, further large scale trials under controlled conditions would be the best way to resolve this. The Temple analysis confirms that if the NO_x reductions shown in the Imperial modelling were borne out in practice, PCTs would be a highly cost-effective tool in tackling air pollution. The risks of harmful by-products can be analysed further in these trials to ensure that the conditions under which they may form can be fully predicted and avoided.

In light of these conclusions, EIC recommends that:

- The forthcoming Defra Air Quality Strategy includes an assessment of the potential role of PCTs
- Funding from the new Clean Air Fund is made available for a number of controlled large scale trials in selected high-pollution areas and that for investigations into potential by-product formation are made.
- AQEG releases an update to its 2016 report acknowledging the additional findings of the Imperial College research.

Annex 1: Titanium dioxide-based coatings for the abatement of nitrogen oxides in air – A report by Imperial College London

I. Aims

I. **Provide an overview of TiO_2-based coatings for the abatement of nitrogen oxides in air, how this technology works, and the current methods for assessing their activity.**

II. **Provide a comprehensive review of recent and notable literature on TiO_2-based coatings for the abatement of nitrogen oxides, and their potential applications in photocatalytic concretes, paints and asphalts.**

III. **Provide a comprehensive review of the field trials on the use of TiO_2-based coatings for abating nitrogen oxides in air carried out in Belgium, France, England, Italy, the Netherlands, the Philippines, the USA and Denmark.**

IV. **Using accurate experimental data, model the potential impact of TiO_2-based coatings for abating nitrogen oxides in a London street canyon scenario.**

V. **Identify the knowledge gap in this field of research and provide recommendations for future work.**

II. Introduction

Nitrogen oxides: Environmental Impact and Regulations in the UK

Nitric oxide (NO) and nitrogen dioxide (NO_2) are gases that are released into the atmosphere when fossil fuels are burned (e.g. petrol/ diesel in a car engine, natural gas in a domestic boiler, power station etc) (Nitrogen Dioxide in the United Kingdom - UK Air Quality Expert Group, 2004). Together, NO and NO_2 are called NO_x, and their emissions cause a wide range of health and environmental problems. NO_x compounds are responsible for ground level ozone and urban smog; created by their photochemical reactions with volatile organic compounds (VOCs). Short-term exposure to high levels of NO_x can cause a range of adverse health effects including exacerbated asthma, inhibited lung function and mortality (UK plan for tackling roadside nitrogen dioxide concentrations: An overview, 2017). Long-term exposure reduces life expectancy (lung, heart and circulatory conditions). NO_x also adversely impacts on the environment. It is a major contributor to acid rain, which harms forests, crops and aquatic life (Carp, Huisman and Reller, 2004).

The burning of fossil fuels releases both NO and NO_x into the atmosphere; however, some sources, such as diesel, release a higher proportion of NO_2 (up to ~25% NO_2 content in NO_x). This is particularly relevant, as NO_2 is between five and twenty five times more toxic than NO (Folli et al., 2015). Road transport is the largest source of NO_x emissions in the UK, contributing 49% of total emissions in the year 2000 (Nitrogen Dioxide in the United Kingdom - UK Air Quality Expert Group, 2004).

In order to improve air quality, the UK and EU have set limits on NO_2 levels: (i) an hourly limit of 200 $\mu g.m^{-3}$ (~0.1 ppmv) that should not be exceeded more than 18 times per calendar year and (ii) an annual average limit of 40 $\mu g.m^{-3}$ (~0.02 ppmv) (EU First Daughter Directive - 99/30/EC). The UK government planned to meet these targets by the year 2005; however, these targets are not achieved in highly polluted and congested areas such as Glasgow, Leeds, Birmingham, Southampton and London. Over the past five years, the annual average NO_2 level at roadsides in London have consistently remained above 50 $\mu g.m^{-3}$ (more than 25% over the specified limit of 40 $\mu g.m^{-3}$) (London Datastore, 2017). The European Commission has issued the UK with a final warning for consistently failing to meet these targets (Neslen, 2017). Achieving the hourly and annual mean limits on NO_x across the whole of London, and other urban areas across the UK, is extremely challenging and high on the political agenda (Barratt, Carslaw and Green, 2012).

Nitrogen Oxide Abatement Strategies in the UK

In the UK, road transport is the largest source of NO_x emissions. In order to reduce these emissions and meet their air quality targets the UK Government intends to end the sale of all conventional cars and vans by 2040, and by the year 2050, have fully transitioned to zero emission vehicles (e.g. electrically powered, hydrogen powered etc) (The Clean Growth Strategy: Leading the way to a low carbon future, 2017). The UK government recently published their strategy for tackling roadside NO_2 (UK plan for tackling roadside nitrogen dioxide concentrations: An overview, 2017). In this report, the UK government outlined several strategies, which included: (i) investing £1 billion in ultra low emission vehicles and the infrastructure for re-charging electrically powered vehicles, (ii) investing £1.2 billion for improving the infrastructure for cycling and walking, (iii) committing £100 million for new buses and retrofits of older buses (equipment that removes ~90% of NO_x emissions), (iv) £89 million of previous investment in the Green Bus Fund, which has helped bus companies and local authorities put over 1,200 new low carbon buses on the roads and (v) awarding over £27 million since 2013 to retrofit ~3,000 of the oldest vehicles (mainly buses) through the Clean Bus Technology Fund and the Clean Vehicle Technology Fund (UK plan for tackling roadside nitrogen dioxide concentrations: An overview, 2017). However, now that the European Commission has issued the UK with a final warning, there is now a pressing need for the UK to meet their air quality targets in the short term. The UK government will consider a range of innovative options, explore new technologies, and has set up an implementation fund (~£255 million) to support local authorities improve air quality.

The Environmental Industries Commission (EIC) recently published a report on the technology options for tackling air pollution (A clear choice for the UK: Technology options for tackling air pollution - The Environmental Industries Commision, 2015). They looked at five options in detail: (i) Replacing 300,000 diesel cars with electric vehicles (as envisioned by the Low Carbon Vehicle Partnership Roadmap - UK Department of Transport), (ii) Replacing 90,000 diesel cars with new Euro 6c diesel cars, (iii) Retrofitting 10,000 old buses with diesel particulate filter (DPF) and selective catalytic reduction (SCR) systems, (iv) Switching 3,000 electricity generators on urban construction sites from red diesel to renewable diesel and (v) Applying titanium dioxide-based coatings (that degrade NO_x in air under the action of

UV light) along a highly polluted road. The report modelled the potential reductions in NO_x emissions of each technology, and provided an in-depth techno-economic cost analysis. The EIC found that the most cost-effective strategy for reducing NO_x emissions in the short term was to retrofit buses, and cost less than £7,000 per tonne of NO_x. In the medium term, the EIC found that replacing diesel cars with Euro 6c diesel cars will be more cost effective; considering the benefits in fuel economy coupled with future fuel price increases. However, the EIC also found that TiO_2-based coatings were a potentially low cost and effective strategy for reducing NO_x emissions (< £40,000 per tonne of NO_x).

Titanium dioxide-based coatings for Nitrogen Oxide Abatement

Titanium dioxide (TiO_2) is the naturally occurring oxide of titanium. It is used in a wide range of applications (e.g. as a white pigment in paint, a UV blocker in sunscreen, a food colorant etc) (Chen and Selloni, 2014). TiO_2 is a photocatalyst and can oxidise organic matter under the action of light; including cancer cells, bacteria and viruses (Fujishima, Zhang and Tryk, 2008). This can only occur when TiO_2 is excited with UV light (or more specifically, light greater than or equal to the bandgap energy) (Mills and Le Hunte, 1997). When this occurs, electrons in TiO_2 are excited to a higher energy level (the conduction band) leaving behind positive holes (the valence band). In TiO_2, these electrons possess sufficient potential energy to reduce oxygen in air into superoxide radicals (O_2^-), and holes possess sufficient potential energy to oxidise water in air into hydroxyl radicals (OH•) (Fujishima, Rao and Tryk, 2000). These radicals are highly reactive and can break down organic matter.

The most thermodynamically stable crystal structure of TiO_2 is rutile (Hanaor and Sorrell, 2010); however, the meta-stable anatase crystal structure is formed at lower temperatures and typically shows higher levels of photocatalytic activity (Luttrell et al., 2014). Rutile and anatase are excited with UV light of wavelengths ≤413 nm and ≤388 nm respectively (which respectively facilitates the absorption of ~8.2% and ~5.3% of the solar spectrum in power terms). Some commercially available TiO_2 photocatalysts contain both anatase and rutile; indeed, one of the most studied photocatalysts, P25 Evonik, contains both anatase and rutile (~80: 20 ratio of anatase: rutile) (Ohno et al., 2001).

TiO_2 is used in a wide range of photocatalytic products, including self-cleaning windows (Pilkington NSG - Activ™, Saint-Gobain - Bioclean, PPG - Sunclean), self-cleaning tiles (TOTO - Hydrotect) and air purification devices (Hoover, electriQ, De'Longhi, Green UV etc). There are also many potential photocatalytic applications of TiO_2, which include the conversion of water into renewable hydrogen fuel (Zhang, Chen and Bahnemann, 2009), the conversion of carbon dioxide into renewable fuels and carbon-based feedstocks (Jia et al., 2017), water remediation (Gaya and Abdullah, 2008) and antimicrobial surfaces (Page, Wilson and Parkin, 2009); however, another potential application, and the focal point of this report, are photocatalytic TiO_2-based coatings for the abatement of NO_x in polluted air. The core of this idea is to incorporate TiO_2 onto building materials, where under the action of UV light, ambient NO_x gases will be oxidised into benign compounds. Various products have been examined; including photocatalytic concretes, paints and asphalts. In addition to oxidising NO_x gases in air, these coatings can also oxidise sulphurous oxides, ammonia and VOCs into benign compounds (Guerrini, 2012).

Japan has been at the forefront of developing practical applications for TiO_2-based photocatalytic compositions for many years now. The Photocatalysis Industry Association of Japan (PIAJ) claimed sales of over $500 million p.a. in the period 2005-2010. The current global market growth for photocatalytic compositions increased from $1.4 billion in 2013 to

nearly $1.5 billion in 2014, and is estimated to be valued at nearly $1.6 billion in 2015. The total market for photocatalyst products is forecast to grow at a compound annual growth rate of 12.6% over the next five years, reaching a market value of ~$2.9 billion by 2020 (Gagliardi, 2015).

Reaction Pathways and Products Formed

Devahasdin et al. studied the oxidation of NO gas on P25 TiO_2 under UV illumination (Devahasdin et al., 2003). They found that NO is oxidised sequentially from NO to nitrous acid (HONO), to NO_2, to nitric acid (HNO_3), by OH• formed on TiO_2. O_2^- is also formed on TiO_2, and reacts with water to form hydroperoxyl (HO_2), and can directly oxidise NO to HNO_3 (Laufs et al., 2010). Ballari et al. studied the oxidation of mixtures of NO and NO_2 gas on TiO_2-based photocatalytic concrete (Ballari, Yu and Brouwers, 2011). They found that the conversion of NO to NO_2 decreased as the relative humidity increased and attributed this to the competing absorption of water. Over the range of conditions investigated, they found that the rate of conversion of NO to NO_2 increased linearly with light intensity. In NO: NO_2 gas mixtures, they found that the kinetics of NO oxidation was faster than NO_2 oxidation. Bahnemann et al. studied the oxidation of NO on P25 TiO_2 and developed a detailed rate law (Dillert et al., 2013).

Various studies have shown that reactions of NO_2 on TiO_2 under UV illumination can result in the net formation of HONO; a harmful respiratory irritant (Langridge et al., 2009). They found that a competing reduction process can occur, where photo-generated electrons on TiO_2 reduce NO_2 to NO_2^-, which reacts with water to form HONO. Gustafsson et al. showed that aqueous aerosols of P25 TiO_2 under UV irradiation can convert NO_2 and water into HONO with high yield (Gustafsson et al., 2006). They surmised that mineral dusts containing significant amounts of titanium dioxide may be a potentially significant source of daytime tropospheric HONO. In a follow up study, Gustafsson et al. showed that hydrogen peroxide is co-produced alongside HONO (Beaumont, Gustafsson and Lambert, 2009). Ndour et al. investigated the reaction of NO_2 on Saharan and Arizona dust, which contain significant levels of TiO_2 (up to ~5 wt.%) (Ndour et al., 2008). No reaction was observed in the dark; however, under UV light, NO_2 levels dropped and HONO was formed. Langridge et al. studied the reaction of NO_2 on commercially available TiO_2-based self-cleaning windows (Langridge et al., 2009). Under UV irradiation (0.6 $mW.cm^{-2}$) they found that between 50 - 70 % of the NO_2 gas stream (~0.07 ppmv) was converted into HONO. Monge et al. studied the reaction of NO_2 on a range of TiO_2/SiO_2 composite coatings (Monge, D'Anna and George, 2010). They found that HONO was formed with yields ranging between ~3 and 36% depending on sample composition and oxygen levels. Gandolfo et al. studied the photocatalytic reactions of NO_2 (0.04 ppmv) on photocatalytic paint (Gandolfo et al., 2015). The photocatalytic paints (ALLIOS) contained anatase TiO_2 (TITANE P2). The efficiency of NO_2 removal increased with the amount of TiO_2 in the paint (0 - 7 wt.% studied). In all reactions, Gandolfo et al. observed the formation of NO and HONO. A maximum conversion of NO_2 to HONO (15%) and NO (33%) was observed at a relative humidity of 30%. Their calculations showed that under irradiation (UVA = 0.9 $mW.cm^{-2}$) a steady state level of HONO (~6 ppbv) would be reached that is almost 4 times higher than the HONO released by regular paint (1.6 ppbv). In a follow up study, Gandolfo et al. studied the effect of wall temperature on the reaction of NO_2 (0.04 ppmv) with photocatalytic paint (Gandolfo et al., 2017). They found that the efficiency of NO_2 removal increases linearly with temperature, which was coupled with an increase in HONO formation.

Laufs et al. studied the reactions of NO, NO_2 and their mixtures on photocatalytic paints under simulated atmospheric conditions (Laufs et al., 2010). Two paints (StoPhotosan NO_x dispersion paint) of different colour (white and blue) and TiO_2 content (Kronos, C-doped anatase TiO_2) were examined. Fast photocatalytic conversion of NO and NO_2 was observed on the photocatalytic paints; no activity was observed in the reference paints that did not contain TiO_2. Nitrous acid (HONO) was formed in the dark on all the paints studied; however, it was efficiently decomposed under irradiation on the photocatalytic paints. Humidity had a significant effect on the concentration of HONO; both the formation of HONO in the dark and its photocatalytic decomposition in the light increased with humidity. From their study they estimated a circa 5% reduction in NO_x for a typical street canyon coated with photocatalytic paint. George et al. observed HONO formation when examining the photocatalytic reduction of NO_2 on commercial photocatalytic concrete; however, they found that similar levels of HONO were formed when the sample was absent from the reactor, and thus attributed the formation of HONO to the Teflon lining (George et al., 2016).

Monge et al. found that ozone (O_3) was formed during the reaction of NO_x gases on TiO_2-coated surfaces and (Monge et al., 2010). O_3 is one of the most toxic and ubiquitous air pollutants (Menzel, 1984). They studied the reaction in both steel and Teflon-lined environmental chambers. In both cases O_3 was formed in the presence of NO and UV light when TiO_2 was present. Although an increase in HONO levels was observed, this was temporary and ultimately reduced from ~6 ppbv to < 2 ppbv after 80 mins of UV irradiation. As ozone was formed in both the presence and absence of oxygen, they concluded that ozone was formed from the re-noxification of HNO_3 formed on the surface of TiO_2 during the oxidation of NO_x gas.

In summary, TiO_2 coatings and materials containing TiO_2 (dust etc) can produce unwanted products, such as HONO, in their reactions with NO_x gas; however, in some cases, TiO_2-based coatings show a low propensity to form such unwanted products (Laufs et al., 2010). Patzsch et al. studied the selectivity of the NO_x oxidation reaction, for the various crystal structures of TiO_2 (anatase, brookite and rutile), co-catalysts and dopants (Patzsch et al., 2017). They found that the accumulation of HNO_3 (from the photocatalytic oxidation of NO_x) not only reduces activity by blocking surface sites, but also reduces the selectivity of the oxygen reduction reaction, through the competing back-reduction of HNO_3 to reform the unwanted product, NO_2. They recommended that TiO_2-based coatings should be engineered to achieve higher oxygen reduction efficiencies in order to curtail re-noxification processes. TiO_2-based coatings were recently discussed in a UK AQEG report (Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016). The report highlighted the need for further analysis of side products that can form from photocatalytic reactions on TiO_2 with NO_x. This was echoed in a recent report published by the California Energy Commission (Evaluation of titanium dioxide as a photocatalyst for removing air pollutants - California Energy Commision, 2008).

Protocol for Measuring Photocatalytic Activity

Of the various techniques for measuring NO_x concentrations, the most prevalent is the chemiluminescence method. It is based on the chemiluminescent reaction of NO with O_3 to form electronically excited NO_2, which fluoresces. The instrument consists of an O_3 generating lamp, a catalyst (typically molybdenum oxide) and a photomultiplier. The instrument first measures the ambient NO concentration by sampling air directly. The instrument then passes air over a catalyst, which converts NO_2 into NO, and again measures the NO concentration. The NO_2 concentration is assumed to be the difference between the two measurements. As such, the most significant problem with

chemiluminescence monitors is their inability to directly detect NO_2. It is well known that other gas phase nitrogen containing compounds (e.g. NO_3, HNO_3, and to a lesser extent, HONO) are converted by molybdenum oxide catalysts to NO, and are therefore misinterpreted as being NO_2. Dunlea et al. compared the NO_x gas concentrations measured using the chemiluminescence method against research grade techniques and found that the chemiluminescence method over-estimated the NO_2 concentration on average by 22% (Dunlea et al., 2007). Villena et al. carried out a similar study and found strong interferences using the chemiluminescence method under both simulated smog conditions and in the field (Villena et al., 2012). However, the chemiluminescence method remains the most widespread and economical method for measuring NO_x concentrations.

The International Organization for Standardization (ISO) have standardised protocol for measuring the NO_x abatement activity in TiO_2-based coatings (previously BS ISO 22197-1:2007, now superseded by BS ISO 22197-1:2016). In brief, the TiO_2-based coating (~5 x 10 cm) is exposed to the model pollutant (NO = 1 ppmv, 3 $L.min^{-1}$) at a constant relative humidity (50%) within a reactor of specified dimensions for 30 mins in the dark, 5 hrs under ultraviolet light (UVA, 300 - 400 nm, 1 $mW.cm^{-2}$) and 30 mins in the dark. Changes in NO are measured using the chemiluminescence method. With knowledge of: (i) the amount of NO absorbed during the initial dark period, (ii) the amount of NO converted into NO_2 and NO_3^- in the light, and (iii) the amount of NO_x desorbed during the final dark period - the NO_x abatement activity can be calculated. These results are typically represented as percentages of NO removed, NO_2 formed and total NO_x removed. In some cases, the mass of NO and total NO_x removed is also calculated (typically in $mg.m^{-2}.hr^{-1}$). In rare cases, the NO removed is expressed as a deposition velocity ($m.s^{-1}$), which is a useful measure that can be compared with tests carried out under different NO_x gas concentrations, flow rates and sample areas (NOTE: it does not account for differences in light intensity, relative humidity etc) (Boonen et al., 2015). In rare cases, the quantum efficiency (activity per incident photon) of NO reduction is presented (Yang et al., 2017). Of note, ISO protocol states that samples should be washed with water after testing, so that the amount of HONO and HNO_3 that resided on the surface of the TiO_2-based coating can be determined from the washings by ion chromatography; however, this aspect of the ISO is rarely carried out (Mills, Hill and Robertson, 2012).

It should be noted, in the field of photocatalysis, a wide range of photochemical reactions are routinely examined (e.g. the conversion of water into renewable hydrogen fuel, the conversion of carbon dioxide into renewable fuels etc). However, ISO protocol has only been established for a handful of those reactions (Mills, Hill and Robertson, 2012). As such, those working in the area of TiO_2-based coatings for NO_x abatement are at an advantage, as there is well established, rigorous protocol for measuring sample activity. This protocol facilitates the fair comparison of sample activity between research groups in academia and industry. This does not mean that the ISO method for measuring NO_x abatement activity does not have its faults, and there are some groups that believe the ISO method can be improved. Ifang et al. found that samples measured under ISO protocol showed contrastingly different levels of activity under atmospheric conditions (Ifang et al., 2014). They attributed this to the high levels of NO used in the test (ISO NO = 1 ppmv vs typical ambient NO in a polluted city < 0.1 ppmv). Mills and Elouali found that the build up of surface nitrates caused a gradual decrease in sample activity, and expressed concerns over the use of such coatings for indoor applications (where regular washing with water to remove surface nitrates is unlikely) (Mills and Elouali, 2015). Mills et al. also noted that highly active coatings, which exhibit quantum efficiencies of ca. > 1.5%, would remove all the NO from the inlet stream (i.e. in such a case, the ISO test would under-predict sample activity) (Mills, Hill and Robertson, 2012). Although the area of the coating can be decreased and the sample re-measured,

overall, the system will not distinguish differences in activity between samples of high photon efficiency (e.g. >1%) due to mass transfer effects. Mills et al. also recognised that the concentration of the pollutant used by this standard (NO = 1 ppmv) is higher than what is typically observed in a polluted city; however, they felt that operating at lower concentrations would increase the likelihood of unwanted mass transfer effects on the reaction kinetics of NO removal.

Various TiO_2-based coatings have been developed for abating nitrogen oxides in air; including photocatalytic concretes, paints and asphalts. We now provide a comprehensive review of recent and notable literature of each application in turn.

Photocatalytic Concrete

Poon and Cheung investigated the photocatalytic NO abatement of TiO_2 intermixed in concrete paving blocks (Poon and Cheung, 2007). Their study focused on using recycled materials. NO abatement increased with block porosity, and with the addition of crushed recycled glass. Three types of TiO_2 were examined: P25 Evonik (formerly Degussa), anatase and rutile. Concrete blocks containing P25 were more active in removing NO than blocks containing anatase or rutile. Activity increased with P25 content, from ~2.5 $mg.m^{-2}.hr^{-1}$ at 2% to ~4.0 $mg.m^{-2}.hr^{-1}$ at 10%. After allowing the concrete to age for 90 days, an 8% reduction in activity was observed. In a follow up study, Chen and Poon investigated the effect of glass colour in photocatalytic blocks made with crushed recycled glass additives (Chen and Poon, 2009). In this study, NO abatement activity was measured in accordance with ISO protocol. Chen and Poon found that using clear recycled glass additives resulted in higher activity in their photocatalytic cement (~3.0 $mg.m^{-2}.hr^{-1}$). Guo and Poon also studied the effect of: (i) replacing sand with glass cullets and (ii) diluting white cement with ground granulated blast-furnace slag or metakaolin in photocatalytic cements containing P25 TiO_2 (2 wt.%) (Guo and Poon, 2013). The use of glass cullets had a positive impact on NO abatement activity (lighter coloured/transparent cullets showed more substantial improvements). Concretes containing ground granulated blast-furnace slag showed slightly higher NO abatement activity than cements containing metakaolin. The addition of pigments caused significant reductions in activity. Harsh abrasion resulted in no obvious deterioration in activity. Their best performing samples showed NO removal rates above 5 $mg.m^{-2}.hr^{-1}$. Poon et al. also studied the performance of photocatalytic concrete intermixed with P25 (5 wt.%) or concrete with a surface spray-coating of P25 (~60 $g.m^{-2}$) (Guo, Ling and Poon, 2017). Activities were measured using ISO protocol and also at a variety of NO flow rates, NO concentrations, relative humidities, light intensities and light sources. Spray-coated concrete was more active than inter-mixed concrete. Under ISO conditions, spray-coated samples showed a NO reduction of ~7 $mg.m^{-2}.hr^{-1}$ and an overall NO_x reduction of ~60%, and inter-mixed concrete showed a NO reduction of ~3 $mg.m^{-2}.hr^{-1}$ and an overall NO_x reduction of ~30%. Similar NO abatement was observed under solar simulated light, but decreased substantially under indoor fluorescent light. No substantial loss in activity was observed with harsh abrasion.

In accordance with ISO protocol, Hüsken et al. assessed the NO removal activity of five commercially available TiO_2 powders in cement (Hüsken, Hunger and Brouwers, 2009). Four cements contained anatase TiO_2, and one contained C-doped anatase TiO_2. They found that some TiO_2 products could achieve mean NO reduction rates of ~40%, whereas other TiO_2 products showed almost no appreciable NO abatement activity. The cement containing C-doped TiO_2 showed some visible light activity (500 - 640 nm), and could reduce NO levels by ~4% at an irradiance of 2 $mW.cm^{-2}$. The addition of a red pigment into the mortar caused a substantial reduction in the photocatalytic activity of the cement.

Hassan et al. studied the abrasion and wear resistance properties of photocatalytic cement (3 - 5 wt.% ultrafine TiO_2), and its effect on photocatalytic performance for NO abatement (Hassan et al., 2010). Abrasion and wearing were simulated in the laboratory using a loaded wheel tester. After 20,000 cycles, the measured rut depth in the concrete samples was minimal (< 1 mm). Photocatalytic NO abatement was measured in accordance with ISO protocol. Before the abrasion test, concrete containing 3 wt.% TiO_2 showed an ~18% reduction in NO, and concrete containing 5 wt.% TiO_2 showed an ~27% reduction in NO. After the abrasion test, some activity was gained in the 3 wt.% TiO_2 concrete (~25% NO reduction activity) and lost in the 5 wt.% TiO_2 concrete (~24% NO reduction activity).

Ballari et al. studied the NO abatement activity of commercially available concrete paving (Ballari et al., 2010). In addition to ISO protocol, they studied the reaction at various initial NO concentrations and flow rates in order to develop a kinetic model. Under ISO conditions they observed an ~25% reduction in NO, ~5 % formation of NO_2 and ~20 % reduction in NO_x. In a follow up study, Ballari et al. studied the photocatalytic degradation of various NO and NO_2 gas mixtures over a wide range of humidities, light intensities and gas concentrations (Ballari, Yu and Brouwers, 2011). When the relative humidity was increased from 10 to 70%, NO removal activity decreased from ~90% to ~50%. At low concentrations of NO (0.1 ppmv), no substantial NO abatement was observed; however, at higher concentrations of NO (1.0 ppmv), a ~43% reduction in NO was observed.

Folli et al. studied the effect of various ions, ionic strength and pH on the formation of cement pastes with TiO_2 (2 wt.%) (Folli et al., 2010). Two commercially available anatase TiO_2 powders were examined; one nano-sized and the other micro-sized. It was not stated if their photocatalytic measurements were in accordance with ISO protocol; however, their preliminary results showed that photocatalytic cement with nano-sized TiO_2 (~31% NO reduction) was more active than cement with micro-sized TiO_2 (~25% NO reduction).

Chen and Chu examined concretes formed with nano-sized anatase TiO_2 and activated carbon (Chen and Chu, 2011). Measurements were seemingly not in accordance with ISO protocol; however, both the NO and NO_2 reduction activities were measured. They found that fresh samples showed high NO and NO_2 reduction rates (~78% and ~59% respectively). After significant wear, the concrete became discoloured, and the activity towards NO and NO_2 reduction decreased (~38% and ~26% respectively).

De Melo et al. studied photocatalytic concrete blocks of various mortar thickness (3 - 10 mm), TiO_2 content (3 - 10 wt.%) and type (anatase/ rutile) (De Melo et al., 2012). Taking the case of a 3 mm thick mortar, NO_x removal activity increased with TiO_2 content in both anatase and rutile-type blocks; increasing from ~27 to 44% with an increase in anatase content from 3 to 10 wt.% and increasing from ~24 to 37% with an increase in rutile content from 3 to 10 wt.%. The photocatalytic concrete was then placed in the field for a year (a road in the city of Florianópolis, Brazil). Subsequent re-examination in the laboratory showed that the NO_x removal activity decreased by 5 - 20%. They estimated, from meteorological and environmental conditions typical of Florianópolis in spring, that one square meter of photocatalytic pavement could remove ~210 mg of NO_x per day.

Shen et al. investigated photocatalytic pervious concretes for the dual purpose of storm water management and air pollutant removal (Shen et al., 2012). The NO removal activity was not measured in accordance with ISO protocol. Plain pervious concretes showed NO reductions of <10%; however, photocatalytic concretes showed NO reductions between 40 and 98%. After four months of weathering (Pullman, Washington), substantial losses in activity were observed.

Sugrañez et al. studied the effect of varying the composition of mortar (sand and water/cement ratio) for a fixed weight of cement and TiO_2 (P25, 1 wt.%) in photocatalytic cement (Sugrañez et al., 2013). NO removal activity was measured in accordance with ISO protocol, where they observed overall NO_x reduction levels between 20 and 25%. It was generally observed that more highly macro-porous concretes were more active. Little difference in activity was observed in changing the curing age from 28 to 90 days.

Pérez-Nicolás et al. studied the effect of various mortars on the activity of photocatalytic cements that contained P25 TiO_2, Fe-doped TiO_2 or V-doped TiO_2 (Pérez-Nicolás et al., 2017). The use of Fe-doped or V-doped TiO_2 did not result in any substantial improvement in visible light activity, where NO reduction levels ranged between ~30 - 40% under UV light and ~20% under visible and solar light. Cements containing air lime and high alumina were the most active and showed the lowest levels of NO_2 production.

Zouzelka and Rathousky compared the activity of photocatalytic spray-coatings of P25 TiO_2 (6.8 $g.m^{-2}$) and Protectam™ FN2 (contains P25, 5 $g.m^{-2}$) on concrete and plaster (Zouzelka and Rathousky, 2017). Coatings were ~10 µm thick. Activity was measured under ISO protocol in addition to conditions more akin to outdoor applications (i.e. lower NO and NO_2 concentrations etc). Coatings of Protectam™ FN2 were more active than P25. ISO tests showed overall NO_x reductions of 12% for Protectam™ FN2 on concrete and 24% on plaster, and NO reductions of 8% for P25 on concrete and 16% on plaster. There was no substantial formation of HONO, where the majority products were surface nitrates and HNO_3. Samples coated with Protectam™ FN2 were placed on a wall in the proximity of a heavily-trafficked thoroughfare in Prague (~30,000 vehicles a day) for two years. No substantial loss in NO_x abatement activity was observed upon their re-examination after this period.

Yang et al. studied the activity and stability of quartz-supported TiO_2 coatings (Yang et al., 2017). Samples were examined in accordance with ISO protocol, where a typical sample showed a ~45% reduction in NO, ~25% formation of NO_2 and a ~20% overall reduction in NO_x. Yang et al. also determined the quantum efficiency (activity per incident photon) of NO reduction, which increased from 0.4 - 0.8% as the TiO_2 loading was increased. When samples were repeatedly washed, a partial loss in activity and selectivity for nitrate formation (i.e. the NO_2 yield increased) was observed.

The photocatalytic NO_x abatement activities of TiO_2-based concretes are summarised in Table 4.

Table 4: Summary of photocatalytic NO_x abatement activities of TiO_2-based concretes

Product	TiO_2 type	ISO*	NO reduction	NO_2 formed	NO_x reduction	Reference
Concrete	P25 (2%)	no	~2.5 $mg.m^{-2}.hr^{-1}$	*ns*	*ns*	(Poon and Cheung, 2007)
	P25 (10%)	no	~4 $mg.m^{-2}.hr^{-1}$	*ns*	*ns*	(Poon and Cheung, 2007)
	anatase	yes	~7%†, ~3 $mg.m^{-2}.hr^{-1}$	*ns*	*ns*	(Poon and Cheung, 2009)
	P25 (2%)	yes	~14%†, ~6 $mg.m^{-2}.hr^{-1}$	*ns*	*ns*	(Guo and Poon, 2013)
	P25 (5%)	yes	~7%†, ~3 $mg.m^{-2}.hr^{-1}$	*ns*	~30%	(Guo and Poon, 2017)
	P25 spray coating (60 gm^{-2})	yes	~16%†, ~7 $mg.m^{-2}.hr^{-1}$	*ns*	~60%	(Guo and Poon, 2017)
	anatase	yes	~40%, ~18 $mg.m^{-2}.hr^{-1}$†	*ns*	*ns*	(Hüsken, Hunger and Brouwers, 2009)
	ultrafine TiO_2 (3%)	no	~18%	*ns*	*ns*	(Hassan et al., 2010)
	ultrafine TiO_2 (3%)	no	~27%	*ns*	*ns*	(Hassan et al., 2010)
	ns	yes	~25%, ~11 $mg.m^{-2}.hr^{-1}$†	~5%	~20%	(Ballari et al., 2010).
	ns	yes	~43%, ~19 $mg.m^{-2}.hr^{-1}$†	~8%	~35%	(Ballari, Yu and Brouwers, 2011)
	anatase - nano-sized	*ns*	~31%	*ns*	*ns*	(Folli et al., 2010)
	anatase - micro-sized	*ns*	~25%	*ns*	*ns*	(Folli et al., 2010)
	anatase - nano-sized	no	~78%	*ns*	*ns*	(Chen and Chu, 2011)
	anatase - nano-sized (3%)	no	*ns*	*ns*	~27%	(De Melo et al., 2012)
	rutile - nanorods (3%)	no	*ns*	*ns*	~24%	(De Melo et al., 2012)
	P25 (1%)	yes	~25%, ~11 $mg.m^{-2}.hr^{-1}$†	~5%	~20%	(Sugrañez et al., 2013)
	P25 (2.5%)	no	~40%	~8%	~32%	(Pérez-Nicolás et al., 2017)
	P25 spray-coating (6.8 $g.m^{-2}$)	yes	*ns*	*ns*	~24%	(Zouzelka and Rathousky, 2017)
	Protectam™ FN2 (5 $g.m^{-2}$)	yes	*ns*	*ns*	~16%	(Zouzelka and Rathousky, 2017)
	anatase hydrosol (0.1 g)	yes	~45%, ~20 $mg.m^{-2}.hr^{-1}$†	~25%	~20%	(Yang et al., 2017)

*measured in accordance with ISO protocol (either 22197-1:2007 or ISO 22197-1:2016), ns = not stated, nm = not measured, † = calculated herein if sufficient information was present in the article.

Photocatalytic Paint

Maggos. et al. studied the NO_x abatement of photocatalytic paints inside a stainless steel (30 m^3) environmental chamber (Maggos, Bartzis, Leva, et al., 2007). The conditions inside the chamber, such as temperature (23 °C), relative humidity (20 - 50%) and light irradiance (~0.4 $mW.cm^{-2}$ of UV light), were made similar to those found in a real world setting. The NO_x concentration inside the chamber was initially set at 0.22 ppmv, similar to urban outdoor levels. Two types of TiO_2 photocatalytic paints were tested; a mineral silicate paint and a water-based styrene acrylic paint. The mineral silicate paint reduced NO levels by 74% (~0.5 $mg.m^{-2}.hr^{-1}$) and NO_2 levels by 27%, and the water-based styrene acrylic paint reduced NO levels by 91% (~0.7 $mg.m^{-2}.hr^{-1}$) and NO_2 levels by 71%. Control paints, without TiO_2, had no substantial effect on removing NO (< 10 %). A decrease in relative humidity from 50% to 20% resulted in up to four-fold enhancements in activity.

Salthammer and Fuhrmann investigated the activity of a photocatalytic paint towards a range of compounds including CO, NO_2 and formaldehyde (Salthammer and Fuhrmann, 2007). The rutile TiO_2-based paint was applied (350 $mg.m^{-2}$, 100 - 250 µm thick coating) onto the walls of a glass chamber (1 m^3). The NO abatement was not measured in accordance with ISO protocol. No change in CO levels were observed; however, NO_2 levels reduced by ~10% from 0.56 to 0.51 $mg.m^{-3}$. The concentration of formaldehyde decreased over a 6 hr testing period from ~1.4 to ~0.35 $mg.m^{-3}$.

Águia et al. studied how the components of paint impact on the NO_x removal activity in photocatalytic paint (Águia et al., 2011a). They found that extenders, such as $CaCO_3$, impair photoactivity, especially when water is involved in mixing the components. Organic components typically impair performance for a transient period of time (ca. 100–250 hr). Águia et al. then evaluated the photocatalytic NO_x removal activity of various commercially available TiO_2 materials (Evonik, Kemira, Kronos, Millennium, Sachtleben and Tayca) in both pressed-powder and within vinyl water-based paint (Águia et al., 2011b). The NO_x abatement activity was measured in accordance with ISO protocol. Pressed-powders of VLP7101 (Kronos) were the most active and showed a 94% NO reduction, 37% NO_2 formation and 57% overall NO_x reduction. All materials showed substantially lower activity in the form of paints, where, for example, VLP7101 (Kronos) showed a 27% NO reduction, 16% NO_2 formation and 11% overall NO_x reduction. Pressed-powders consistently showed higher activity than paints, which was explained in part by the TiO_2 content (100 wt.% in pressed-discs, 17 wt.% in paints). Águia et al. defined the yield as the cross product between NO reduction % and the selectivity for forming nitrate. The highest yields in paints were found in PC500 and PC105 from Millennium and UV100 from Sachtleben (all ca. 0.15).

Ângelo et al. studied the NO_x removal activity of paints in both a laboratory and outdoor setting (Ângelo, Andrade and Mendes, 2014). Two types of photocatalytic paint were examined: one composed of P25 (Evonik) and the other of PC500 (CristalACTiV™). The NO_x abatement activity was measured in accordance with ISO protocol. The most active paint contained PC500 (CristalACTiV™), and showed a ~70% NO reduction, ~42% NO_2 formation and ~28% overall NO_x reduction. Under outdoor tests (NO stream of 0.2 ppmv), all photocatalytic paints showed reductions in NO above 80%. The most active paint contained PC500 (CristalACTiV™), showing reductions in NO above 95%.

In relation to indoor air purification, Auvinen and Wirtanen studied photocatalytic paints for the decomposition of formaldehyde and VOCs (Auvinen and Wirtanen, 2008), Yu and Brouwers studied photocatalytic wallpaper for NO_x abatement (Yu and Brouwers, 2009), Mo et al. (Mo et al., 2009) and Wang et al. (Wang, Ang and Tade, 2007) reviewed photocatalytic coatings for removing VOCs and Costarramone et al. examined a range of commercially available air purifiers for removing VOCs (Costarramone et al., 2015).

Poon et al. investigated the impact of laboratory accelerated weathering on the activity of TiO_2-based photocatalytic paints (Guo, Maury-Ramirez and Poon, 2015). The paint was composed of a novel transparent photocatalytic coating, applied onto an architectural mortar by brushing 3 layers of an aqueous dispersion of TiO_2 (PC-S7, CristalACTiV). The NO_x abatement activity was examined in a similar manner to ISO protocol (with the exception of relative humidity being 30% instead of 50%). Two weathering processes were investigated; (i) a lab-simulated façade weathering process and (ii) carbonation. The lab-simulated process mimics the weathering process caused by rainwater and sunlight on the façade of a building. Samples were subjected to a series of wet and dry, and dark and night cycles; equivalent to approximately 10 - 20 years of weathering (compared with conditions found in Hong Kong). Accelerated carbonation was carried out in a carbonation chamber for 70 days. Before weathering, the photocatalytic paint showed a NO_x abatement activity of 259.3 $mmol.m^{-2}.h^{-1}$. After weathering, no significant reduction in NO_x abatement activity was observed (~2% loss in activity). These paints showed similar NO_x removal activity under visible light irradiation, and thus the potential for indoor applications. No obvious loss in photocatalytic activity was observed after carbonation (Guo, Maury-Ramirez and Poon, 2016).

The photocatalytic NO_x abatement activities of TiO_2-based paints are summarised in Table 5.

Table 5: Literature summary of the photocatalytic NO_x abatement activity of TiO_2-based paints

Product	TiO2 type	ISO*	NO reduction	NO_2 formed	NO_x reduction	Reference
Paint	*ns* (styrene acrylic paint)	no	~91%, ~0.7 $mg.m^{-2}.hr^{-1}$†	~71%	*ns*	(Maggos, Bartzis, Leva, et al., 2007)
	rutile	no	*nm*	~10%, ~0.04 $mg.m^{-3}$	~10%	(Salthammer and Fuhrmann, 2007)
	VLP7101 Kronos™ C-doped anatase (17%)	yes	~27%, ~12 $mg.m^{-2}.hr^{-1}$†	~16%	~11%	(Águia et al., 2011b)
	PC500 CristalACTiV™ anatase (18%)	yes	~70%, ~31 $mg.m^{-2}.hr^{-1}$†	~42%	~28%	(Ângelo, Andrade and Mendes, 2014)
	StoClimasan	yes	~14%, ~6 $mg.m^{-2}.hr^{-1}$†	10.4%	3.5%	(Mills and Elouali, 2015)

*measured in accordance with ISO protocol (either 22197-1:2007 or ISO 22197-1:2016), ns = not stated, nm = not measured, † = calculated herein if sufficient information was present in the article.

Photocatalytic Asphalt

Chen and Liu investigated the photocatalytic NO_x abatement of nano-sized anatase TiO_2 embedded within MAC-70# asphalt (Chen and Liu, 2010). The effects of surface friction, humidity and light intensity on the NO_x removal activity were systematically investigated. NO_x reduction levels between 6 and 12% were observed. In a follow up study, Chen et. al investigated the use of N-doped TiO_2 embedded on the surface of asphalt (Chen et al., 2017). NO_x abatement activity was measured in both the laboratory and the field. The activity of asphalt containing N-doped TiO_2 was higher than asphalt containing pure TiO_2. N-doped TiO_2 endued visible light activity. NO_x removal activity was measured at various wavelengths; decreasing from ~30% in the UVA to ~14% in the green. Results from field tests and simulations suggested a 13 month service life of N-doped TiO_2 asphalt.

Carneiro et al. developed synthetic methods for preparing photocatalytic asphalt (Carneiro et al., 2013). TiO_2 (P25 Evonik) was either added to the asphalt mixture or spray-coated onto the asphalt surface. The NO_x removal activity was not measured.

Liu et al. investigated the photocatalytic NO_2 removal of nano-sized anatase TiO_2 cross-linked onto the surface of asphalt (Liu et al., 2015). The NO_2 abatement activity was not measured in accordance with ISO protocol. A photocatalytic reduction of NO_2 of up to 90% was observed under optimal conditions (NO_2 ~10 ppmv). Preliminary outdoor tests showed NO_2 reductions of ~50%.

Wang et al. developed a new method of coating TiO_2 onto asphalt pavements (Wang et al., 2016). Pulverized TiO_2-cement mortar was used as the spreading material, which is bonded to the asphalt pavement using an epoxy resin. Various commercial TiO_2 products were examined (4 wt.%). The NO_x abatement activity was measured in accordance with ISO protocol. Using nano-sized anatase, NO reductions of up to 67% were observed. A test section of the photocatalytic asphalt was constructed at the Institute of Highway Engineering Aachen. The activity of a drilled core from the test track was assessed in the laboratory and showed a NO reduction of ~25%. In a follow up study, Wang et al. investigated the use of surface coating and pore-filling methods to produce photocatalytic asphalt using nano-sized anatase (Wang et al., 2017). Photocatalytic NO reduction was similar in both materials (~42%); however, pore-filled asphalt showed more prolonged activity. Polishing the asphalt resulted in a significant loss of activity, with NO reduction rates falling to ~10 and 15% for surface coated and pore-filled asphalt.

The photocatalytic NO_x abatement activities of TiO_2-based asphalts are summarised in Table 6.

Table 6: Literature summary of the photocatalytic NO_x abatement activity of TiO_2-based asphalts

Product	TiO_2 type	ISO*	NO reduction	NO_2	NO_x	Reference
Asphalt	nano-sized anatase	yes	~67%, ~30 $mg.m^{-2}.hr^{-1}$†	*ns*	*ns*	(Wang et al., 2016)
	micron-sized anatase: rutile	yes	*~14%, ~6 $mg.m^{-2}.hr^{-1}$†*	*ns*	*ns*	(Wang et al., 2016)
	nano-sized anatase	yes	~42%, ~19 $mg.m^{-2}.hr^{-1}$†	*ns*	*ns*	(Wang et al., 2017)

*measured in accordance with ISO protocol (either 22197-1:2007 or ISO 22197-1:2016), ns = not stated,
† = calculated herein if sufficient information was present in the article in the article.

Summary

Most studies were of photocatalytic concretes for applications on roads and pavements. The activity was not measured in accordance with ISO protocol for a significant portion of studies. Few studies discussed the net formation and yield of NO_2; despite this being a more toxic compound than NO. However, some studies were thorough, and measured activity under ISO protocol in addition to a range of relative humidities, light intensities, flow rates, NO: NO_2 ratios and concentrations (Ballari, Yu and Brouwers, 2011). Of note, most studies did not monitor the potential formation of hazardous side products such as HONO and O_3.

For products measured under ISO protocol, reductions in NO ranged from ~7 to 45% (i.e. ~3 to 20 $mg.m^{-2}.hr^{-1}$) in concretes, ~14 to 70% (i.e. ~6 to 31 $mg.m^{-2}.hr^{-1}$) in paints, and ~14 to 67% (i.e. ~6 to 30 $mg.m^{-2}.hr^{-1}$) in asphalts. Durability was often not assessed; however, generally speaking, concretes were more robust in comparison to asphalt, and retained their activity after years of testing.

In the following section we will chronologically review field trials of TiO_2-based coatings for abating nitrogen oxides in air carried out in Belgium, France, England, Italy, the Netherlands, the Philippines, the USA and Denmark.

III. Field trials

Antwerp - 2004

Boonen and Beeldens, of the Belgian Road Research Centre (BRRC), carried out a field trial in Antwerp using concrete paving stones coated with anatase TiO_2 (Boonen and Beeldens, 2013). The anatase was intermixed within the wearing layer (~8 mm thick). The paving stones were first analysed in the laboratory (in accordance with ISO protocol, 2007), and showed a ~20% reduction in NO_x gas (at a relative humidity of 30%). At higher relative humidity, the NO_x gas reduction decreased (to < 5% at a relative humidity of 70%). In their field trial, an area of 10,000 m^2 was coated with photocatalytic paving stones, on the parking lanes of a main road axe in Antwerp (between 2004 and 2005). The parking lanes (4.5 m wide), were spaced on either side of a main road (51 m wide) (Beeldens, 2006). The paving stones were removed after five years and re-examined in the laboratory (again, in accordance with ISO protocol, 2007), and showed on average a 60% reduction in NO gas. They found that the deposition of pollutants (such as NO_3^- build-up, dirt etc) on the surface of the concrete causes a decrease in activity. This activity was regained by washing the paving stones with water.

Paris - 2004

Within the framework of the EU PICADA project (Photocatalytic Innovative Coverings Applications for Depollution Assessment), Maggos et al. conducted a field trial on three artificial street canyons in Guerville, near Paris, from July to September 2004 (Maggos et al., 2008). They studied the efficacy of photocatalytic cement (Italcementi Group; mineral binder treated with 3 wt.% TiO_2 and sand) for NO_x abatement, which was applied to the surface of walls (~5 m high and ~20 m long). Two walls were spaced 2 m apart, which formed an artificial street. Three artificial streets were examined for three scenarios: (i) no cement was applied, (ii) cement without TiO_2 was applied and (iii) cement with TiO_2 was applied. At select times, a polluting source was added to the artificial street. When the pollution source was emitting, NO_x values were significantly higher, reaching values as high as 150 ppbv. NO_x values in TiO_2 treated street were between ~40 to ~80% lower than in the reference streets. Maggos et al. also conducted a study of photocatalytic paints in a car park (920 m^3) in La Défense, West of Paris (Maggos, Bartzis, Liakou, et al., 2007). The ceiling of the car park was coated with an acrylic TiO_2-containing photocatalytic paint (320 m^2). UVA lamps were installed, and showed intensities ranging from 0.01 to 0.47 $mW.cm^{-2}$, depending on the location. The closed area was fed with car exhaust gases. As soon as the system reached steady state, the UV lamps were turned on for five hours. The difference between the final and initial steady state concentrations showed a 19% reduction in NO (~0.47 $mg.m^{-2}.hr^{-1}$) and a 20% reduction in NO_2 gas (~0.58 $mg.m^{-2}.hr^{-1}$). A control test, using paint that did not contain TiO_2, showed a < 5% reduction in NO_x gas. Maggos et al. also measured the change in concentration of other pollutants including SO_2, CO and VOCs, such as benzene and toluene; however, a detailed analysis on the impact of the coating on these pollutants was not provided in their report.

Tower Hamlets - 2005

Barratt conducted a field trial on photocatalytic paint in the London Borough of Tower Hamlets on an eastern wall of the Sir John Cass School (Barratt, 2007). NO_x levels were measured from September 2005, six months before the coating was applied in April 2006, until December 2006. Although Barratt found that NO_x levels decreased by 19% after the coating was applied, the decrease in NO_x levels during daylight hours was comparable to the non-daylight control. Therefore, they could not attribute this decrease in NO_x level to the photocatalytic paint. Colvile et al. corroborated with his conclusion (Colvile et al., 2007), and surmised that the observed decrease in NO_x levels were most likely due to seasonal variations caused by changes in wind speed and direction. Moreover, their modelling showed that the outdoor benefits of treating a single building would be restricted to a thin layer of air very close to the painted façade.

Camden - 2007

Barratt et al. conducted a field trial on the efficacy of a TiO_2-based paint in the London Borough of Camden (Barratt, Carslaw and Green, 2012). The western wall (135 m^2) of the inner courtyard of St. Martin's College was painted with a developmental water-based product (PCX-S7). The site was chosen as it represents an area of London with relatively high NO_x concentrations (up to 500 ppbv). Before the coating was applied, the NO_x gas levels were assessed over a 16-month period (starting September 2007). The coating was applied in March 2009, and the efficacy towards NO_x gas reduction was assessed over a nine-month period. In August 2010 the coating was boarded up, and the NO_x gas levels were assessed for a further five months.

Without filtering their data, there was no apparent reduction in NO_x gas levels. Barratt et al. found that during non-north westerly winds, air sampled by the analysers had not been in contact with the treated surface or for a long enough time for any significant abatement to occur. However, when they filtered their data to include periods of north westerly winds between 6 am and midnight, there was some evidence of a reduction in NO_x levels (between 5% and 10% reduction where NO_x levels decreased by up to 8 ppbv). After the coating was boarded up, NO_x gas levels increased, which was indirect evidence of a NO_x abatement effect in the coating.

Rome - 2007

Guerrini conducted a field study on photocatalytic cement based coatings (Italcementi) in the Umberto I tunnel in Rome (Guerrini, 2012). Pollution levels were monitored from May 2007. In August 2007, two layers of the photocatalytic coating was applied using an airless spraying technique (covering an area of 9,000 m^2 inside the tunnel), and a UVA lighting system (2 $mW.cm^{-2}$) was installed. Laboratory testing showed that these cement based coatings were particular effective in reducing NO_x levels, showing a ~90% reduction in NO_x gas (it was unclear if these measurements were carried out in accordance with ISO protocol). Comparing NO_x levels measured in the centre of the tunnel with NO_x levels measured at nearby monitoring stations, they concluded that was a 23% mean reduction in NO_x levels. Mean NO_2 levels in the centre of the tunnel also decreased by 19% during this period.

Hengelo - 2008

Ballari et al. conducted a field trial on Castorweg street in Hengelo, Netherlands using photocatalytic concrete blocks (Ballari and Brouwers, 2013). The photocatalytic concrete was produced by Struyk Verwo Infra, which consisted of an active upper layer (5 mm thick) intermixed with TiO_2. One end of the street was paved using photocatalytic concrete (5 m wide and 150 m long), and the other end was paved using regular concrete (5 m wide and 100 m long). Both ends of the street possess near identical traffic volume and pollution levels. NO_x levels were monitored from December 2008. The paving was installed in November 2009, however; no significant decrease in NO_x levels were observed. Therefore, in order to increase the efficacy of the photocatalytic concrete, an additional coating was applied in May 2010, which consisted of a suspension of TiO_2 (C-doped TiO_2; Kronos International) that was spray-coated onto the street (4 wt.% TiO_2 aqueous suspension; 50 L used to coat 750 m^2). However, after ~3 months, the coating was lost due to vehicular wear and weathering. A second, more durable coating was applied in September 2010 that functioned for ~11 months.

Laboratory tests (measured according to ISO protocol) showed that these spray coatings could achieve NO_x reduction levels of ~40%. However, after substantial weathering, these coatings showed NO_x reduction levels as low as ~3%. Measurements in the field, during periods where the coating was active (i.e. had not been removed due to weathering) showed that NO_x concentrations were lower, on average, by 19% (considering the whole day) and 28% (considering only afternoons) than the control street. Moreover, under ideal weather conditions (high radiation and low relative humidity), the effect was more significant (NO_x decrease as high as 45% observed).

Manila - 2009

Borlaza et al. conducted a large-scale field trial on photocatalytic paint in and around the Guadalupe MRT station, Manila in 2009 (Borlaza, 2013). The paint was composed of a styrene acrylic water-based paint that contained ultra-fine TiO_2 (7.5 wt.%). NO_x levels were monitored at 18 different sites; 13 of which were coated with the photocatalytic paint and five of which were painted with regular paint. An area totalling ~6,000 m^2 was coated with photocatalytic paint, making this one of the largest trials to date. The locations showed varying degrees of confinement, exposure to prevailing winds, and sunlight. Almost all locations were chosen to reflect the air that people breathe; either as pedestrians, commuters, or workers in this highly polluted area (between 138,000 to 184,000 vehicles passing through this site per day; where traffic accounts for ~80% of NO_x emissions in Metro Manila). Average NO_2 levels in this area are high (126 $\mu g.m^{-3}$, ~60 ppbv); however, after the photocatalytic coatings were applied, this was reduced by up to 23%.

Brussels - 2011

Within the framework of the European Life+ funded project PhotoPAQ (Demonstration of Photocatalytic remediation Processes on Air Quality), Gallus et al. investigated the effect of photocatalytically active mortars within the Leopold II tunnel in Brussels (Gallus et al., 2015). In their first study, a cement-based coating (Italcementi, TX-Active™ Skim Coat) was spray-coated onto the side walls and ceiling of a 70 m long section of the tunnel in August 2011. UV lighting systems were installed, which emitted a low average irradiance of ~0.06 $mW.cm^{-2}$ (over the 315 - 420 nm range). NO_x gas levels were measured at both ends of the coated section, in June 2011 (before the coating was applied) and in September 2011 (after the coating was applied). In a second trial, a 160 m long section of the tunnel was coated in January 2013 using a more active version of the cement-based coating (Italcementi, TX-Active™ Skim Coat - Boosted), and the UV intensity was increased to ~0.16 $mW.cm^{-2}$.

In contrast to laboratory studies of fresh samples, both field tests showed no observable reduction of NO_x in the tunnel. Switching the UV lamps on/off did not result in any systematic steps in the concentration difference between the two measurement sites. After the field trial, sections of the coating were removed from the tunnel and re-assessed in the laboratory (Boonen et al., 2015). Boonen et al. found that the high levels of pollution inside the tunnel had passivated the surface of the coating (e.g. soot, brake dust, etc), and caused the NO_x removal activity to decrease substantially. For the case of a single layer cement-based coating, a pristine sample showed a deposition velocity of 0.22 $cm.s^{-1}$, whereas a tunnel coating showed deposition velocity of 0.07 $cm.s^{-1}$. Moreover, the NO_2 yield increased substantially from 8% in a pristine sample to 265% in a tunnel coating. This showed that the tunnel coatings were inundated with NO_x species, which desorbed during laboratory testing. However, the activity of these coatings could be recovered by either: (i) exposure to UV light for several days (deposition velocity of 0.16 $cm.s^{-1}$ and NO_2 yield of 33%) or (ii) rinsing with water (deposition velocity of 0.12 $cm.s^{-1}$ and NO_2 yield of 24%).

Based on their results, Gallus et al. concluded that photocatalytic remediation of NO_x in a road tunnel can only be obtained under suitable conditions, and that remediation is not possible in materials that show strong deactivation under highly polluted conditions (such as those used in their field trials) (Gallus et al., 2015). Moreover, they further concluded that the application of photocatalytic coatings will not result in significant remediation at: (i) low UVA irradiance levels (such as those used in their field trials, which were < 0.2 $mW.cm^{-2}$), (ii) high wind speeds and (iii) high humidity levels.

Louisiana - 2011

Hassan et al. assessed the NO_x removal activity of photocatalytic asphalt pavement (Hassan et al., 2013). Anatase TiO_2 nanoparticles (2%) were suspended in an aqueous solution and spray-coated onto the surface of the asphalt (0.05 $L.m^{-2}$). The NO_x abatement activity was not measured in accordance with ISO protocol. They found that the coating was effective in removing both NO_x and SO_2 pollutants from the air, with efficiencies ranging from 31 -55% for NO_x and 4 - 20% for SO_2. Untreated asphalt showed negligible activity. An abrasion test was performed in the laboratory using a loaded wheel tester. After 20,000 cycles a substantial decrease in activity was observed (up to 70% loss in activity). Field tests were conducted on the campus of Louisiana State University (Field and Laboratory Investigation of Photocatalytic Pavements - Gulf Coast Research Center for Evacuation and Transportation Resiliency, 2011). NO_x levels were monitored at both the coated and uncoated sections. Ambient NO_x levels were measured 10 days before the application of the coating, and 10 days thereafter. Measured NO concentrations were significantly lower after the TiO_2 coating was applied. Nitrates were collected from the coated (~0.3 $mg.L^{-1}$) and uncoated (< 0.05 $mg.L^{-1}$) areas as further evidence of photocatalytic oxidation of NO_x. A maximum SO_2 reduction of ~20% was also observed. Hassan et al. estimated that the use of photocatalytic asphalt will marginally increase fabrication costs by ~11%.

Wijnegem - 2011

As part of the Interreg Eco2 profit project (Interreg Eco2 profit, 2010), Boonen and Beeldens carried out another field trial using photocatalytic concrete on the Den Hoek 3 industial site in Wijnegem, near Antwerp in March 2011 (Boonen and Beeldens, 2014). The concrete was applied to roads, pavement, bicycle lanes and parking spaces. They again investigated the use of TiO_2 (4 wt.%) intermixed in the surface layer of concrete, and also the use of aqueous dispersions of TiO_2 that were spray-coated onto the surface of the cement. For the intermixed TiO_2, they applied an exposed aggregates surface finish; some sections were cured and others were not. NO_x reduction was measured on site in August 2011, five months after the concrete was applied. Rather than measuring ambient NO_x gas levels, an enclosed area of the concrete was examined within a portable testing unit. Sections of concrete that were cured showed a 27% reduction in NO_x gas (from 1 ppmv) using ambient sunlight (UV content ~1 - 1.1 $mW.cm^{-2}$). Non-cured sections showed higher reductions in NO_x gas (~48% reduction) even though ambient sunlight at the time of testing was less intense (UV content ~0.6 $mW.cm^{-2}$). The non-cured section was re-examined a year later in August 2012 and showed a 34% reduction in NO_x gas under ambient sunlight (UV content ~0.8 $mW.cm^{-2}$). It was clear that the curing compound inhibited the photocatalytic action of the concrete; however, over time this activity was regained due to the wearing of the curing compound and re-exposure of the TiO_2 layer beneath. In October 2012 an aqueous TiO_2 dispersion (Eoxolit™, 40 $g.L^{-1}$) was also applied on the surface in some parts of the roads (dose of ~1 L per 5 m^2 for a total of 800 m^2); however, the dispersion did show any significant NO_x removal activity.

In addition, a concrete pavement was constructed in the industrial zone of Duwijckpark in Lier (January 2012), which contained TiO_2 intermixed in the surface layer (Boonen and Beeldens, 2014). The NO_x removal activity was examined 20 months after concreting (August 2013), and showed a ~12% reduction in NO_x gas under a low intensity of ambient sunlight (UV content ~0.26 $mW.cm^{-2}$).

Copenhagen - 2012

Folli et al. conducted a field trial using photocatalytic paving on a central street in Copenhagen, Gasværksvej, located in the Vesterbro district (Folli et al., 2015). The test area (800 m^2) consisted of two pavements (each 2 m wide) that sandwiched the road (200 m long). One side was coated with photocatalytic paving (100 m) and the other side was coated with ordinary concrete (100 m). The photocatalytic paving was provided by Starka Betongindustrie, where the top 10 mm consisted of earth moist concrete inter-mixed with TiO_2 (40 $kg.m^{-3}$ of concrete).

The paving stones were first examined in the laboratory to evaluate their photocatalytic activity; however, they were not examined in accordance with ISO protocol. Folli et al. observed high reductions in NO gas concentrations (up to 78%) with low amount of NO_2 formation. The paving blocks were installed in June 2012, and testing was carried out between April 2012 and August 2013. This gave two months of measurements (April - May 2012) without the application of the photocatalyst, which served as blank test, and 14 months of measurements after the coating was applied (June 2012 - August 2013). After the paving stones were applied, NO levels in the proximity of the photocatalytic paving were consistently ≤40 ppbv throughout the year, with the exception of four days that occurred around the time of winter solstice. On the other hand, NO levels in the proximity of the un-coated paving showed higher average NO concentrations and surpassed 40 ppbv on 16 occasions (independent of the time of year). However, no significant reductions in NO_2 levels were observed between the photocatalytic and control sites. During periods where UV irradiance exceeded 600 $kJ.m^{-2}.day^{-1}$ (about six months of the year), a strong correlation between NO concentration and UV irradiance was observed in the vicinity of the photocatalytic paving; where the monthly difference between the photocatalytic paving and control areas were as high as 22%. Within this period, NO levels measured at solar noon often showed instantaneous NO abatement (e.g. at summer solstice a 45% reduction in NO was observed, which corresponded to a total NO_x abatement >30%).

The Hague - 2013

Kerrod et al. conducted a field trial in Koningstunnel, The Hague, in 2013 using an ultrafine and transparent TiO_2 spray-coating (Kerrod and Mcintyre, 2014). A 150 m trial section of the 650 m long tunnel was coated with the photocatalyst (Boysen Paints KNO_xOUT™ Clear). Lab trials showed that the photocatalyst could function in low light levels (< 0.1 $mW.cm^{-2}$). A UVA light system was installed, which possessed intensities of 0.1 $mW.cm^{-2}$ on the tunnel walls and 0.06 $mW.cm^{-2}$ on the tunnel ceiling. Laboratory tests showed that the coating could reduce NO_x levels by up to ~80% (and NO_2 by ~50%) under 1 $mW.cm^{-2}$ UVA light. Field trials showed that the photocatalytic coatings reduced NO levels by 20%, but showed no appreciable reduction in NO_2. Kerrod et al. also measured the accumulation of nitrates on strips placed in the tunnel, where these nitrates accumulated from the oxidation of NO_x species from the air. From measuring nitrates, they calculated that between 10 and 55% of NO was removed from the air, which was in line with their measurements of NO levels on site. Towards the end of the trial, concrete slabs from the tunnel wall and ceiling were recovered and their NO_x abatement was measured in the laboratory. Using parameters similar to ISO protocol a ~40% reduction in NO_x was observed, with no appreciable change in NO_2 levels.

Discussion

Since 2004, field trials on both photocatalytic concretes and paints have been conducted in a number of cities across the globe.

Comparing the three tunnel studies carried out in Rome - 2007 (Guerrini, 2012), Brussels - 2011 (Boonen et al., 2015; Gallus et al., 2015), The Hague - 2013 (Kerrod and Mcintyre, 2014); contrasting results are observed. In the Rome trial, significant reductions in both NO and NO_2 levels were observed. In The Hague trial, only reductions in NO were observed. And in the Brussels trial, no significant reductions in NO_x were observed. These differences may be explained in part by the order of magnitude difference in UVA light levels used across the three studies (Rome ~2 $mW.cm^{-2}$, The Hague ≤ 0.1 $mW.cm^{-2}$, Brussels ≤ 0.16 $mW.cm^{-2}$). After the field trial in Brussels, samples were taken from the site and re-assessed in a laboratory environment, where it was found that soot, dust and other particulates had accumulated on the surface of these coatings; resulting in a loss of function (Boonen et al., 2015). Their photocatalytic function could be restored with extensive UV treatment or washing with water. Gallus et al. commented on this, and recommended that higher UV light intensities (≥ 1 $mW.cm^{-2}$) should be used in future tunnel studies to avoid surface passivation (Gallus et al., 2015). Moreover, Gallus et al. added that photocatalytic products should be examined on a small scale, under real tunnel conditions, before attempting a mass trial.

Barratt conducted two field trials on photocatalytic paints in London; one in Tower Hamlets - 2005 (Barratt, 2007) and the other in Camden - 2007 (Barratt, Carslaw and Green, 2012). In both trials, relatively small areas were coated (e.g. 135 m^2 in the Camden trial), and no significant reduction in NO_x was observed (NOTE: during the Camden trial the coating was boarded up and NO_x levels increased, which was indirect evidence of a NO_x abatement effect). Modelling by Colvile et al. showed that the outdoor benefits of such a small-scale application would be limited to a small area close to the coating (Colvile et al., 2007), and that this problem will be exacerbated at locations where dispersion and ventilation was too strong to see an effect (e.g. Tower Hamlets, where the detector was placed 5 m from the wall). Colvile et al. recommended that larger, and more sheltered areas should be coated in future trials. Maggos et al. conducted a small-scale field trial on photocatalytic paint in which they created artificial street canyons in Paris - 2004 (Maggos et al., 2008). A recent UK AQEG report (Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016) commented on this field trial and argued that the reductions in NO_x that Maggos et al. observed were unrealistic due to the high aspect ratio of the canyon. However, we argue that the evidence from this field trial should not be disregarded as there may be adventitious cases where such photocatalytic coatings can be deployed (e.g. between tall buildings in close proximity to each other). Maggos et al. also conducted a small-scale field trial in a car park in La Défense, west of Paris - 2004 (Maggos, Bartzis, Liakou, et al., 2007). The UK AQEG report also commented on this field trial and argued that the study provided little detail on their analysis. We find the article to be thorough in their methodology and analysis of the NO_x abatement effect of the TiO_2 coating. Borlaza et al. conducted a large scale field trial of photocatalytic paint (6,000 m^2) in Manila - 2009 (Borlaza, 2013) and observed reductions in ambient NO_2 levels of up to 23%.

Field trials on photocatalytic concrete paving were carried out in Antwerp - 2004 (Boonen and Beeldens, 2013), Hengelo - 2008 (Ballari and Brouwers, 2013), Wijnegem - 2011 (Boonen and Beeldens, 2014) and Copenhagen - 2012 (Folli et al., 2015). During the Antwerp trial, NO_x gas levels were only measured on site for a single day (insufficient to draw any reliable conclusions). However, the paving stones were removed after five years and re-examined in the laboratory; and showed a high efficacy for NO_x gas reduction. In the Wijnegem trial, the activity of an enclosed area of the paving was examined within a portable testing unit, rather than measuring changes in ambient NO_x levels. Moreover, spray-coatings did not show any significant NO_x abatement (unlike the Hengelo trials). The Hengelo and Copenhagen trials were similar in that one end of a street was paved with photocatalytic concrete, and the other end with regular concrete. However, in the Hengelo trial, the photocatalytic paving showed no observable NO_x abatement. A spray-coated layer of TiO_2 was later applied, resulting in a significant NO_x abatement effect; however, the coatings were not durable (a complete loss in activity was observed in less than a year). In the Copenhagen trial, significant reductions in NO were attributed to the photocatalytic paving, yet, NO_2 levels remained constant. This study was commented on in a recent UK AQEG report (Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016), where it was argued that plots of UV irradiance against NO concentration showed no obvious relationship (Folli et al., 2015); however, the authors argue that this plot shows how NO levels near the photocatalytic paving were consistently ≤40 ppbv throughout the year (with the exception of four days) and NO levels near the un-coated paving showed higher average NO concentrations and surpassed 40 ppbv on 16 occasions.

In general, NO_x reduction levels measured in the laboratory were substantially higher than those measured on site; and can be attributed to various environmental factors found in field trials such as: (i) a lower concentration of ambient NO_x gas, (ii) a lower level of UVA light, (iii) often higher levels of relative humidity, (iv) higher wind speeds (i.e. gas flow rates) etc. In most field trials, NO_x levels were measured before and after the photocatalytic coatings were applied. However, few field trials were as thorough as the Camden trial (Barratt, Carslaw and Green, 2012) in measuring ambient NO_x levels for a year before applying the photocatalytic coating (as ambient NO_x levels are highly influenced by the weather). Moreover, in some field trials, a split site was used, such as those carried out in Hengelo - 2008 (Ballari and Brouwers, 2013) and Copenhagen - 2012 (Folli et al., 2015), where the photocatalytic material was placed on one site and a control material was placed on the other site. Although strong evidence for NO_x abatement was observed in the sites coated with photocatalytic materials, it is more difficult to validate observed reductions in NO_x gas using a split site - as differences may be caused by environmental factors such as: (i) differences in traffic volume/ local sources of pollution, (ii) differences in wind direction/ speed caused by the surrounding architecture etc.

A recent UK AQEG report (Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016) covered the field trials in Paris - 2004, Camden - 2007, Hengelo - 2008, Brussels - 2011 and Copenhagen - 2012, but did not cover the trials, as we have, in Antwerp - 2004, Tower Hamlets - 2005, Rome - 2007, Manila - 2009, Louisiana - 2011, Wijnegem - 2011 and The Hague - 2013. The UK AQEG report surmised that there was little current evidence to suggest the widespread use of photocatalytic surfaces will reduce ambient concentrations of NO_2, despite overwhelming evidence from laboratory based trials. They also argued that photocatalytic surfaces will only reduce NO_x levels in the vicinity of the treated surface and will not significantly reduce NO_2 concentrations in the surrounding air. We believe that this will be the case for small-scale trials, where the area of the photocatalytic coating is too small to sufficiently reduce NO_x levels in the surrounding air. However, large-scale trials carried out in Rome - 2007 (9,000 m^2 coating) and Manila

(6,000 m^2 coating) showed significant decreases in NO_2 in the surrounding air. The UK AQEG report rightfully highlighted the lack of studies on the potentially harmful side-products that can arise from the use of photocatalytic coatings, such as the formation of formaldehyde from the partial degradation of adsorbed VOCs, and the need for more durability tests. This was recently highlighted by Costarramone et al. in their study of indoor air-purifiers, which similarly use TiO_2-based photocatalyst to drive the photocatalytic oxidation of pollutants in air (Costarramone et al., 2015). They found that some indoor air-purifiers only partly oxidised VOCs in air, resulting in temporary increases in formaldehyde. However, more active indoor air-purifiers could completely oxidise VOCs and their by products, such as formaldehyde, to carbon dioxide.

IV. Modelling

Previous studies

Moussiopoulos et al. computationally simulated the NO_x abatement effect of TiO_2-based coatings (Moussiopoulos et al., 2008). Their simulations were based on the field trials carried out by Maggos et al., as part of the EU PICADA project, on three artificial street canyons in Guerville, near Paris (Maggos et al., 2008). Moussiopoulos et al. used the numerical model MIMO; a three-dimensional model for simulating microscale wind flow and dispersion of pollutants in built-up areas. Both field trials and simulations indicated an average NO_x reduction of between 50 and 60%.

Churchill and Panesar carried out a life-cycle cost analysis of highway noise barriers designed with photocatalytic cement, and examined their environmental and economic feasibility (Churchill and Panesar, 2013). Assuming a 6 $mg.m^{-2}.hr^{-1}$ NO_x degradation rate in the photocatalytic coating, and a 40-year service life, their study showed that a barrier made from general use cement with a 25 mm thick photocatalytic coating has an annual cost that is 7% higher than regular uncoated general use cement. However, assuming a 20 $mg.m^{-2}.hr^{-1}$ NO_x degradation rate in the photocatalytic coating, a barrier made from general use cement with a 10 mm thick photocatalytic coating is more economical than an uncoated barrier (assuming the cost of mitigating NO_x exceeds ~$9000/tonne).

The potential NO_x reducing effect of TiO_2-based paints, for a London-based scenario, were modelled in a recent UK AQEG report (Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016). Their model assumed a surface resistance of 1000 $s.m^{-1}$ for an uncoated surface (i.e. a deposition velocity of ~0.10 $cm.s^{-1}$) and a surface resistance of 400 $s.m^{-1}$ for a surface coated with photocatalytic paint (i.e. a deposition velocity of ~0.24 $cm.s^{-1}$). Taking a typical London average NO_2 concentration of 35 $\mu g.m^{-3}$, deposition fluxes of ~0.12 and 0.30 $mg.m^{-2}.hr^{-1}$ were predicted for coated and uncoated surfaces respectively. Based on the annual NO_x emission rate, they calculate that an average emission rate of ~1.8 $mg.m^{-2}.hr^{-1}$ occurs in London, which is six times greater than the removal capacity of paint, and surmised that photocatalytic paint would have a small impact on ambient NO_2 levels. The NO_x abatement effect of photocatalytic paint was also simulated for a road in central London (17 m high and 20 m wide). They simulated the case for a street being coated with photocatalytic paint, and the walls of the canyon remain un-coated, and predicted reductions in NO_x of ~0.7%.

Our studies

In this section we model the potential impact of TiO_2-based coatings for the abatement of nitrogen oxides in a London street canyon scenario and provide a cost-benefit analysis. This work was carried out in collaboration with the Temple Group Ltd.

NO_X Abatement

Our model focuses on the exclusive use of photocatalytic coatings and paints, as they have a lower initial cost of implementation compared with photocatalytic concretes. Our model looks at the potential impact of TiO_2-based coatings in winter (January 2016) and summer (June 2016) months in London. During these months, average mean roadside NO_x levels in London were 183.1 $\mu g.m^{-3}$ in January 2016 (NO = 123.1 $\mu g.m^{-3}$, 0.092 ppmv; NO_2 = 60.0 $\mu g.m^{-3}$, 0.029 ppmv) and 118.2 $\mu g.m^{-3}$ in June 2016 (NO = 69.5 $\mu g.m^{-3}$, 0.052 ppmv; NO_2 = 48.7 $\mu g.m^{-3}$, 0.024 ppmv) (London Datastore, 2017). Recent work by Engel et al. have collated the deposition velocities of various TiO_2-based coatings, including paints and concretes (Engel et al., 2015). TiO_2-based acrylic paints showed deposition velocities between 0.66 to 1.5 $cm.s^{-1}$ for NO reduction and 0.32 to 0.58 $cm.s^{-1}$ for NO_2 reduction. It should be noted that these deposition velocities are significantly higher than those used by the UK AQEG in their modelling studies (Paints and Surfaces for the Removal of Nitrogen Oxides - UK Air Quality Expert Group, 2016). Using these deposition velocities, NO_x removal activities are determined herein for winter and summer months in London (see the Appendix: Deposition Velocity). We predict respective NO and NO_2 reduction rates of 5.9 and 1.1 $mg.m^{-2}.hr^{-1}$ for wintertime in London, and NO and NO_2 reduction rates of 3.3 and 0.93 $mg.m^{-2}.hr^{-1}$ for summertime in London.

Our model street canyon consists of a street 1000 m long, 30 m wide, with buildings 20 m high on both sides. Taking a wind speed of 4 $m.s^{-1}$ (London average) flowing parallel to the street, and assuming air does not escape from the canyon, air moves through this canyon at a rate of 2400 $m^3.s^{-1}$ and would take ~250 s to move from one end of the street to the other. In wintertime, this moving volume of air would contain ~295 mg of NO and ~144 mg of NO_2, and in summertime, this moving volume of air would contain ~167 mg of NO and ~117 mg of NO_2.

Let us now consider two scenarios: (i) half the buildings are coated with photocatalytic paint, and (ii) half the buildings are coated with photocatalytic paint and all of the ground is covered with a photocatalytic coating.

In the first scenario, this moving volume of air would be in contact with an area of 80 m^2 of photocatalytic paint per second. In the summertime, the moving volume of air would experience an NO reduction of ~0.073 $mg.s^{-1}$ and NO_2 reduction of ~0.021 $mg.s^{-1}$. On moving from one end of the street canyon to the other, the total NO and NO_2 reductions, in this moving volume of air, would be ~18.3 mg (~11.0 %) and ~5.2 mg (~4.4 %) respectively. In the wintertime, the moving volume of air would experience an NO reduction of ~0.13 $mg.s^{-1}$ and NO_2 reduction of ~0.025 $mg.s^{-1}$. On moving from one end of the street canyon to the other, the total NO and NO_2 reductions, in this moving volume of air, would be ~32.8 mg (~11.1 %) and ~6.2 mg ~ (4.3 %) respectively.

In the second scenario, this moving volume of air would be in contact with an area of 200 m^2 of photocatalytic paint per second. In the summertime, the moving volume of air would experience an NO reduction of ~0.18 $mg.s^{-1}$ and NO_2 reduction of ~0.052 $mg.s^{-1}$. On moving from one end of the street canyon to the other, the total NO and NO_2 reductions, in this moving volume of air, would be ~45.8 mg (~27.5 %) and ~12.9 mg (~11.0 %) respectively. In the wintertime, the moving volume of air would experience an NO reduction of ~0.33 $mg.s^{-1}$ and NO_2 reduction of ~0.062 $mg.s^{-1}$. On moving from one end of the street canyon to the other, the total NO and NO_2 reductions, in this moving volume of air, would be ~81.8 mg (~27.7 %) and ~15.6 mg (~10.8 %) respectively. The results are summarised in Table 7.

Table 7: Summary of the predicted NO_x reductions from our model of a street canyon in London (1000 m long, 30 m wide, with buildings 20 m high on both sides). Scenario (i) half the buildings are coated with photocatalytic paint and (ii) half the buildings are coated with photocatalytic paint and all of the ground is covered with a photocatalytic coating.

Scenario	Season	Activity ($mg.m^{-2}.s^{-1}$)		NO_x reductions in moving volume of gas (2,400 m^3)	
		NO	NO_2	NO	NO_2
(i)	Summer	3.3	0.93	18.3 mg, 11.0%	5.2 mg, 4.4%
	Winter	5.9	1.12	32.8 mg, 11.1%	6.2 mg, 4.3%
(ii)	Summer	3.3	0.93	45.8 mg, 27.5%	12.9 mg, 11.0%
	Winter	5.9	1.12	81.8 mg, 27.7%	15.6 mg, 10.8%

Our predictions in NO_x reductions were determined using deposition velocities, which do not account for changes in light levels. However, studies by Dillert et al. showed that NO reduction kinetics were less strongly affected by changes in light intensity at low NO concentrations, similar to those found in London (Dillert et al., 2013). The deposition velocities used in our calculations were typically measured at a relative humidity of 50% (Engel et al., 2015). Studies by Ballari et al. showed that NO_x reduction kinetics decrease at higher relative humidities (London average ~73%) (Ballari et al., 2010). Laboratory based studies showed that the efficacy of photocatalytic paints for removing NO_x decreases as they accumulate surface nitrates (from the oxidation of NO_x) (Mills and Elouali, 2015). This activity can be restored upon washing (Boonen et al., 2015). Our model does not account for this temporary loss in activity, but rather, assumes that the activity of the coating is maintained by sufficient rainfall (Colvile and Maksimovic, 2017). It should also be noted that our model assumes a non-turbulent flow of air through the canyon; however, air flow modelling studies by Moussisopolous et al. showed that air flowing through a street canyon will be turbulent, and form localised vortexes that will increase the residence time of air; and hence NO_x reduction activity (Moussiopoulos et al., 2008). Therefore, we believe the model we apply herein results in conservative predictions of NO_x reductions for a given deposition velocity.

Some studies have shown that HONO levels increase (a harmful respiratory irritant) during the reaction of NO_2 on TiO_2-based paints (Gandolfo et al., 2015), whereas some studies show the contrary (Laufs et al., 2010). The formation of HONO, and other potential side products, has been neglected in our model; however, we recommend that future studies, carried out both in the lab and field, examine their potential formation and environmental impact.

Poon et al. observed no substantial loss in photocatalytic activity in TiO_2-based paints after accelerated weathering, likened to approx 10 - 20 years of weathering under Hong Kong conditions (Guo, Maury-Ramirez and Poon, 2015). Al-Kattan et al. investigated the release of Ti from paints containing micron and nano-sized TiO_2 particles (Al-Kattan et al., 2013). Panels were exposed to simulated weathering in climate chambers, where they observed a very small release of TiO_2 into water, close to background values (< 1.5 $\mu g.L^{-1}$ over +100 cycles; <0.01% of the total Ti content). Zhang et al. studied to the effect of weathering, pH, rainfall and intensity of rainfall on the release of TiO_2 from paints (Zhang et al., 2017). In all cases, the release of TiO_2 into water was low and ranged between 0.6 - 2.3 $\mu g.L^{-1}$. These results suggest that paints containing nanoparticulate TiO_2 will not release substantial levels of TiO_2 into the environment. Several companies produce TiO_2-based photocatalytic paint, and claim performance lasting up to 15 years (e.g. PPG). However, for our cost analysis, covered in Annex 2, we have chosen a conservative scenario of three years before re-coat, with no loss in activity over this period. It should be noted that this we have taken a conservative view on re-coat time, and should thus cause our cost-performance analysis to also be conservative.

V. Conclusions

TiO_2-based coatings can abate NO_x present in air under the action of light, and can be applied to a range of building materials; including concretes, paints and asphalts. Promising levels of activity have been measured in the laboratory, which has resulted in numerous field trials being carried out across the globe (Belgium, France, England, Italy, the Netherlands, the Philippines, the USA and Denmark).

These field trials have shown varying levels of success, and may be attributed to various factors, including: (i) the activity of the photocatalytic coating used, (ii) the area of coating applied, (iii) the intensity of UV light (in particular, for tunnel trials), etc. Although some trials were inconclusive (e.g. Camden - 2007), it is clear that in other trials, substantial reductions in ambient NO_x levels were observed (e.g. Rome - 2007, Manila - 2009 etc).

This report provides up-to-date and extensive coverage of recent literature and field trials. This report also assesses the potential impact of TiO_2-based coatings on nitrogen oxides in London city air. Activities from recent literature studies were applied to a simple but technically robust street canyon model. We find that air, moving from one side of the street canyon to the other, would experience a significant reduction in NO_x content (up to a 38.5 % reduction in NO_x for both summer and wintertime).

Although the study of TiO_2-based coatings for the abatement of nitrogen oxides is a rich and active field of research, with contributions from academic, industrial and governmental partnerships, this report seeks to identify the knowledge gap that should be filled before this technology can progress. For example, NO_x abatement activity was not always measured in accordance with ISO protocol. Moreover, the conditions of the ISO test are quite dissimilar from those typically observed in the field. What is often observed during an ISO measurement is the conversion of NO to HNO_3, coupled with some steady-state formation of NO_2; giving the false impression that these coatings are net NO_2 producers (NO_2 being a more toxic compound than NO). However, studies by Brouwers et al., carried out in NO and NO_2 mixtures, have shown that TiO_2-based coatings can reduce both NO and NO_2 levels (Ballari et al., 2010; Ballari, Yu and Brouwers, 2011). Laboratory trials of TiO_2-based coatings often show higher levels of nitrogen oxide removal than those examined in the field.

There are a variety of reasons for why this is the case, which include differences in: (i) NO_x levels; where laboratory measurements are often carried out in higher concentrations of NO_x gas than those present in the field, resulting in a more pronounced abatement, (ii) UVA light levels; where in some cases the UVA light intensity used in the laboratory (ISO = 1 $mW.cm^{-2}$) is higher than what is experienced in the field (in particular, during wintertime), (iii) wind speed/ gas flow rate; where laboratory measurements are often carried out at lower flow rates (ISO = 0.2 $m.s^{-1}$) than those observed in the field (e.g. London average wind speed ~4 $m.s^{-1}$), resulting in higher a NO_x residence time and abatement effect and (iv) humidity; where laboratory measurements are often carried out at a lower relative humidity (ISO = 50%) than what is observed in the field (e.g. relative humidity ranges from ~70 - 90% across the UK), where higher performance is often observed at lower relative humidity. Also, many field trials have not assessed the potential formation of toxic side products such as nitrous acid, ozone and formaldehydes (from the oxidation of VOCs), which have been observed in some lab-based studies.

Recommendations

Learning from past field trials, and the recent literature, we believe further field trials are needed in order to more conclusively assess the impact of TiO_2-based coatings for the abatement of nitrogen oxides in air. We make the following recommendations for the future testing and field trials of TiO_2-based coatings:

- ISO protocol: Initial laboratory tests of should be carried out under ISO protocol (22197-1:2016). This should include the examination of surface nitrates, which accumulate on the surface of the photocatalyst from the oxidation of NO_x. By conforming to ISO protocol, comparisons can be made between different studies. We also recommend the examination of photocatalytic activity at a range of NO: NO_2 ratios (as opposed to the solitary analysis of NO in accordance with ISO protocol). This is because urban air contains both NO and NO_2.

- Standardised measures of activity: Measures of activity, in particular those not measured in accordance with ISO protocol, should be expressed in a more comparable format. Rather than simply stating the percentage reduction of NO_x, studies should present the percentage of NO removed, NO_2 formed and NO_x desorbed in the dark. Moreover, studies should express activity as a deposition velocity, which accounts for measurements using different NO_x gas concentrations, flow rates and sample areas (NOTE: it does not account for differences in light intensity, relative humidity etc). For completeness, studies should also present activity for NO removed and NO_2 formed in terms of mass, per unit area, per unit time (e.g. $mg.m^{-2}.hr^{-1}$). Currently, there is no sufficient need to present quantum efficiency (activity per incident photon), as the reaction rate is often more limited by the low concentration of NO_x gas present. However, if the use of visible light active photocatalysts becomes more prevalent, then expressing activity in terms of quantum efficiency will increase in importance.

- Standardised field trials: Field trials have shown varying levels of success. For field trials to be more reliable and comparable, they should be conducted in a standardised manner. At a given site, we recommend that ambient NO_x levels are measured, and meteorological data collected, for ideally a full year before the trial is begun. We therefore do not recommend the use of split sites. If NO_x levels are to be measured using the chemiluminescence method in a geographical area where

the concentration of other nitrogen containing compounds (e.g. NO_3, HNO_3, HONO etc) are suspected/known to be comparable to NO_2, we recommend the use of an alternative method for measuring NO_2 levels (e.g. tuneable infrared laser differential absorption spectroscopy, differential optical absorption spectroscopy etc), as nitrogen containing compounds can interfere with the assessment of NO_2 levels using the chemiluminescence method. Once conditions are known, the proposed photocatalytic material should first be examined in the laboratory under conditions similar to those observed on site (i.e. using typical NO_x concentrations, flow rates/ wind speeds, UVA irradiance, relative humidity, temperature etc) (NOTE: it may be beneficial to examine a larger area of sample than specified in ISO22197-1:2016). Many areas in Europe possess high levels of humidity, which may adversely impact on the activity of photocatalytic coatings. Moreover, annual average NO_x levels, wind speeds and temperatures can differ considerably from those specified in ISO protocol. Field testing should only be carried out if the coating shows significant NO_x abatement under simulated conditions.

- Cost-benefit analysis: Before conducting field trials, a preliminary cost-benefit analysis should be carried out. The product cost, area of coating, durability, NO_x abatement activity and loss in activity over time should be considered in these calculations. For more accurate cost-benefit analyses, meteorological effects should be considered using a robust model (NOTE: certain applications may possess a high initial implementation cost, such as enclosed areas like tunnels, which require the installation of UVA lamps to activate the coatings and regular washing to remove the build up of surface nitrates).

- Side-products: In some studies, the NO_2 yield is not presented (merely NO_x abatement is shown). It is important that studies state the net generation of NO_2, as it is more toxic than NO. Moreover, most field trials have not monitored the side-products that can form from the oxidation of VOCs present in air (some of which are toxic, e.g. formaldehyde, O_3 etc), or the potential formation of HONO (also toxic). We recommend that future field trials monitor the potential formation of these compounds and assess their potential detrimental impact on air quality.

- Classify materials: In the absence of intellectual property issues, studies should report the photocatalyst used in their studies (e.g. pigmentary rutile TiO_2, pigmentary anatase TiO_2, speciality photocatalytic anatase TiO_2, anatase: rutile TiO_2 composite such as P25 Evonik etc) and present some of the fundamental properties of the material (optical bandgap, average particle size and shape, etc).

- Certify commercial products: In a recent study, Costarramone (2015) evaluated the efficiency and harmfulness of a range of commercially available indoor air purifiers. They found that some devices could efficiently degrade VOCs and formaldehyde (a toxic intermediate by-product); however, other devices were net formaldehyde producers (and therefore deemed unsafe). These differences in performance were attributed to differences in product design, photocatalyst used, ventilation etc. Given the results of their study, they pointed out the urgent need for suitable evaluation and certification of indoor air purifiers to validate their effectiveness and safety for consumers. The Industry Association of Japan (PIAJ) certifies photocatalytic products when their performance, usage and other features are recognized as appropriate by the association. We recommend the development of similar certification procedures for commercially available photocatalytic products in the UK.

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Abbreviations

AQEG	Air Quality Expert Group
BRRC	Belgian Road Research Centre
DPF	Diesel Particulate Filter
ISO	International Organization for Standardization
PPBV	Parts Per Billion by Volume
PPMV	Parts Per Million by Volume
PhotoPAQ	Demonstration of Photocatalytic Remediation Processes on Air Quality
EIC	Environmental Industries Commission
NPV	Net Present Value
PIAJ	Photocatalysis Industry Association of Japan
PICADA	Photocatalytic Innovative Coverings Applications for Depollution Assessment
SCR	Selective Catalytic Reduction
UVA	Ultraviolet A (315 to 400 nm)
VAT	Value Added Tax
VOCs	Volatile Organic Compounds

Appendix

Deposition Velocity

In a plug flow reactor, the deposition velocity (*vd*, $cm.s^{-1}$) can be defined as:

$$vd = log_e(c_0 c_i) \times F/A$$

where c_0 is the inlet gas concentration, c_i is the outlet gas concentration, F is the flow rate of the gas ($cm^3.s^{-1}$) and A is the area of the photocatalytic coating (cm^2) (Boonen et al., 2015). This equation can be rearranged to:

$$c_i = c_0 / e^{(A \times vd / F)}$$

For samples measured under ISO protocol, F = 50 $cm^3.s^{-1}$, and A = 50 cm^2; therefore, A/F = 1 $cm.s^{-1}$ and the equation simplifies to:

$$c_i = c_0 / e^{vd}$$

Let's now consider conditions present in London, where the average wind speed (~4 $m.s^{-1}$, F = 1000 $cm^3.s^{-1}$) is far higher than what is applied during the ISO test (~0.2 $m.s^{-1}$, F = 50 $cm^3.s^{-1}$) and NO_x gas concentrations (NO_x = 0.121 ppmv, January 2016) are typically lower than what is applied during the ISO test (NO = 1 ppmv).

Let us now predict the NO_x reduction activity of a TiO_2-based acrylic paint, with respective NO and NO_2 deposition velocities of 1.5 and 0.58 $cm.s^{-1}$ (Engel et al., 2015). The reductions in NO and NO_2 that would be observed, when measured inside an ISO-type reactor, would be 7.2 and 2.9 % respectively. For wintertime in London (January 2016, NO = 123.1 $\mu g.m^{-3}$, 0.092 ppmv; NO_2 = 60.0 $\mu g.m^{-3}$, 0.029 ppmv) (London Datastore, 2017), this corresponds to respective NO and NO_2 reduction rates of 5.9 and 1.1 $mg.m^{-2}.hr^{-1}$. For summertime in London (June 2016, NO = 69.5 $\mu g.m^{-3}$, 0.052 ppmv; NO_2 = 48.7 $\mu g.m^{-3}$, 0.024 ppmv) (London Datastore, 2017), this corresponds to respective NO and NO_2 reduction rates of 3.3 and 0.93 $mg.m^{-2}.hr^{-1}$.

Annex 2: Economic assessment of photocatalytic treatment – A report by Temple Group

Introduction

Temple Group have been commissioned to undertake an update of the economic assessment previously carried out on the costs and benefits associated with a range of mitigation for large-scale pollution reduction in the UK.

The previous study[1] looked at the nitrogen oxides (NO_x) and particulate matter (PM_{10}) reductions which could be achieved for a range of mitigative measures, including:

- Electric vehicles: Replacement of 300,000 diesel cars by electric vehicles as envisioned by Low Carbon Vehicle Partnership (LCVP) roadmap.
- Liquified Petroleum Gas (LPG): 75,000 diesel cars replaced with new LPG cars.
- Euro6c diesels: 90,000 old diesel cars replaced by new Euro6c diesel cars in 2018/19.
- Bus retrofit: 10,000 old buses in cities outside London retrofitted with DPF and SCR technology.
- Renewable diesel: 3,000 electricity generators on urban construction sites switch from using red diesel to renewable diesel.
- Photocatalytic treatment: 200 km of most polluted roads treated with photocatalytic treatment.

The EIC commissioned Imperial College to undertake a detailed review[2] of the field and laboratory trials of photocatalytic coatings to provide an updated assessment of the NO_x reduction potential. This comprehensive review looked at a range of published scientific literature over a range of conditions to assess the effectiveness of photocatalytic coatings as a mitigation option for NO_x. The data collated from this review was then looked at with the aim of replicating London conditions, so as to give an estimation of the real-world effectiveness of photocatalytic coatings as mitigation for NO_x. This review resulted in the selection of a winter and summer scenario with respective NO_x reductions, split into both nitrogen oxide (NO) reduction and nitrogen dioxide (NO_2) reduction potential. Temple have taken the resultant scenario NO_x reduction rates and applied updated costs of application in order to calculate an updated cost of photocatalytic treatment per tonne of NO_x abated.

It should be noted that the scope of this study is limited to the update of the photocatalytic coating aspects. The previous study[1] should be referenced for the details surrounding the other measures and the assumptions utilised.

Methodology

NO_X Reduction of Photocatalytic Coatings

Refer to Imperial College report[2] on Titanium dioxide-based coatings for the abatement of nitrogen oxides in air.

Costs Assessment of Photocatalytic Coatings

The previous economic analysis[1] looked at the capital costs of purchasing the photocatalytic coating, and the ongoing operational costs of applying, and reapplying, the coatings. This updated assessment has been kept consistent with the methodology of the previous assessment in order to maintain comparability to the previous assessment's figures for the other NO_x mitigative options.

The photocatalytic coating's impact has been calculated in comparison to a reference case (what would occur if the technology was not implemented). The cost and reduction in NO_x quantities have then been used to determine the cost per tonne of NO_x. It should be noted that PM_{10}, which was assessed in the previous study, was not included as part of this update.

Two impact timeframes have been explored:

- 2020 – to show what kind of emissions can be mitigated in the near term; and
- 2030 – to show the full impact of introducing photocatalytic coatings in terms of cost and emissions mitigation.

The data were obtained from a range of sources: interviews and information from EIC members validated through desk-based research, the latest UK government information and other data sources (e.g. industry-averaged cost estimation factors).

The costs for application of the photocatalytic coatings will vary significantly depending on the application surface, whether any pre-treatment is required, whether it can be consolidated into general maintenance work, and many other factors. For this reason, low, mid and high cost scenarios have been determined in order to present a range of application costs for comparison. The low cost scenario is based on vehicle spray application rates, on a similar cost basis to the initial study[1,3]. The mid cost scenario is based on average contractor pricing for application of coatings to bitumen and concrete surfacing[4]; whilst the high cost scenario is based on the average cost of application based on composite trade rates for construction sites in London[5]. The low cost scenario is considered feasible for simple applications where vehicle spraying can be implemented without significant preparatory costs, etc. Conversely, the high cost scenario is considered more representative for areas where manual application would be required, which could apply to building application of coatings which cannot be done via vehicular spraying. The mid scenario is presented in the following section for base comparison, which could be viewed as a conservative option, depending on the nature and scale of the surfaces being coated. The low and high scenario results are also included for information of the potential variance in this abatement option.

As far as possible, resource costs have been used, i.e. the costs of technologies without taxation such as value added tax (VAT) and without subsidies being taken into account. This is aligned with the previous study[1], such that all technologies are considered on a level playing field without current government support or duties which might favour some technologies over others.

Government bureaucracy costs for setting up an incentive scheme for the technology options have not been included.

Costs are shown as the net present value (NPV) of each technology scenario. If a technology has a negative net cost, it will cost less to implement the technology over its lifetime than the costs associated with the alternative reference case.

A discount rate has been applied to future costs (as social discount rate of 3.5% per annum, in line with the previous study[1]).

Economic Assessment of Photocatalytic Coatings

Based on the conclusions of the Imperial College review work[2], two scenarios were developed based on study data which most closely matched real-world conditions for London streets. The two scenarios represented summer and winter conditions, which represent the highest and lowest solar radiation rates, as well as the lowest and highest background NO_x concentrations, respectively. Table 8 gives the NO, NO_2 and NO_x reduction rates under summer and winter conditions.

Table 8 Selected NO_x reduction rates for photocatalytic coating application

NO_x reduction rates	Summer	Winter
Paint NO reduction activity (mg/m^2/h)	3.3	5.9
Paint NO_2 reduction activity (mg/m^2/h)	0.9	1.1
Paint NO_x reduction activity (mg/m^2/h)	4.2	7.0

The costs identified for coating purchase and application are detailed in Table 9.

Table 9 Cost estimates and assumptions for coating application

Cost estimates and assumptions	Data	Units
Unit cost of photocatalytic coating	1.2	£ / m^2
Spreading rate for coating application	10	m^2 (area) / l (coating)
Application labour cost – low estimate	1.9	£ / m^2
Application labour cost – mid estimate	5.0	£ / m^2
Application labour cost – high estimate	10.0	£ / m^2
Total cost per application – low estimate	3.1	£ / m^2
Total cost per application – mid estimate	6.2	£ / m^2
Total cost per application – high estimate	11.2	£ / m^2
Re-application rate	3	Years

The costs per tonne of NO_x abated based on NPV using a 3.5% discount rate is shown in Table 10 for the low, mid and high cost scenarios, based on an approximated average NO_x reduction over a given year up until both 2020 and 2030. The NO_x reductions were calculated based on a single canyon study area 1 km long and 30 m wide, with 20 m building heights on each side, with the assumption that the floor and 50% of the walls are coated in order to calculate an effective reduction rate and associated cost.

The derived costs per tonne are assumed to be scalable to the size of the intended application which, for the previous study, was an application over 200 km of road coverage. The reduction costs per tonne of NO_x derived here have been applied to the 200 km of road coverage scenario in order to maintain consistency with the previous study.

Table 10 Net present value cost of photocatalytic treatment per tonne of NO_x abated

Scenario	Data	Units
Low cost scenario to 2020	23,530	£ / tonne of NO_x abated
Mid cost scenario to 2020	40,523	£ / tonne of NO_x abated
High cost scenario to 2020	73,203	£ / tonne of NO_x abated
Low cost scenario to 2030	18,729	£ / tonne of NO_x abated
Mid cost scenario to 2030	32,255	£ / tonne of NO_x abated
High cost scenario to 2030	58,267	£ / tonne of NO_x abated

Tables 11 and 12 show how the revised mid cost scenario cost compares with the cost per tonne of NO_x abated for the other technologies analysed in the 2015 Temple/EIC report[1]:

Table 11 Net present value cost to 2020 of technologies per tonne of NO_x abated

Technology	£/t NO_x abated
Electric cars	2,196,676
Euro 6c diesel car	398,108
Photo-catalytic treatment	40,523
Renewable diesel generators	38,719
Bus retrofit	6,842

Table 12 Net present value cost to 2030 of technologies per tonne of NO_x abated

Technology	£/t NO_x abated
Electric cars	1,073,812
Renewable diesel generators	36,534
Photo-catalytic treatment	32,255
Bus retrofit	5,769
Euro 6c diesel car	-38,355

Conclusions

Based on the NO_x reduction scenarios provided by the Imperial College review[2], an updated cost of application of photocatalytic coatings per tonne of NO_x reduction has been prepared. To allow for the high variance in labour costs in the application process, a range of costs have been provided.

The NO_x abatement rates for the London-esque scenario are 34% higher than in the previous study.

The low cost scenario is in line with the previous application cost scenario; hence the overall cost effectiveness of photocatalytic coatings is higher than in the previous study.

The mid cost scenario is a more conservative scenario in terms of application costs, and includes higher costs than the previous study used; however, with factoring in the higher NO_x reduction rates, the overall cost per tonne is similar to the conclusions of the initial study.

The high cost scenario represents a conservative cost basis which is likely to represent an upper boundary of the application rates for photocatalytic coating.

The overall cost effectiveness of the application of photocatalytic paints as an option for NO_x abatement is considered to be in line with the previous study. However, it is noted that, based on the conclusions of the Imperial College review[2], further work is needed. Further work should investigate both:

- more accurate field trial data to increase confidence in the NO_x reductions achievable; and
- the potential for formation of toxic substances including formaldehyde and nitrous acid.

Endnotes

1. The Environmental Industries Commission (2015). A clear choice for the UK: air quality abatement cost curve analysis.
2. Imperial College (2017). Titanium dioxide based coatings for the abatement of nitrogen oxides in air (reproduced as Annex 1).
3. Pers.Comms. David Williams, Cristal. Re; Numbers for modelling. 27th November 2017.
4. http://www.constructionrates.co.uk/Rate_Gen/Painters@constructionrates.co.uk.html.
5. Turner & Townsend (2016). International construction market survey 2016.

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