AIR QUALITY EXPERT GROUP

Paints and Surfaces for the Removal of Nitrogen Oxides

Prepared for:

Department for Environment, Food and Rural Affairs;
Scottish Government; Welsh Government; and Department
of the Environment in Northern Ireland

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This is a report from the Air Quality Expert Group to the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of the Environment in Northern Ireland, on paints and surfaces for the removal of nitrogen oxides.

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PB14425

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- Suggest priority areas for future work, and advise on Defra's implementation of the air quality evidence plan (or equivalent);
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Contents

Executive Summary

- There is increased interest in the use of outdoor photocatalytic surfaces (surfaces that act as a catalyst when exposed to light) as a means of reducing concentrations of various pollutants; principally nitrogen oxides (NO_x which includes nitrogen monoxide, NO and nitrogen dioxide, NO_2), particularly NO_2.
- There are many examples of materials that use titanium dioxide (TiO_2) to promote photocatalytic reactions including paint, concrete and glass.
- TiO_2 surfaces have been studied extensively in the laboratory and this helps to provide information on the chemical reactions that take place and the reaction products formed, although new information is constantly emerging. Under laboratory conditions photocatalytic surfaces have been shown to effectively reduce concentrations of NO_x.
- Compared with emissions source control, reducing emissions once diluted in the atmosphere is challenging. It is much more difficult to remove pollutants from the atmosphere because of the large volume of the atmosphere compared to the surface area of any potential abatement technology.
- There have been two large EU-funded projects considering these materials in the field: PICADA and Photopaq. The field trials from the former did report considerable reductions in NO_x concentration. However, the PICADA field trials were unrealistic in the sense that tests considered very high surface/volume ratios.
- The more comprehensive and carefully designed field trials carried out as part of Photopaq (street canyon + illuminated tunnel) provide no compelling evidence that these materials result in a reduction in NO or NO_2 concentrations.
- A field trial in London did not show strong evidence of reduced NO_x concentrations due to the photocatalytic surface and it was difficult to discern any clear effect that could be attributed to the influence of the paint.
- Other species are also known to undergo photosensitised reactions on TiO_2 surfaces, with possible consequences for air quality. For example NO_x may be generated from reactions of ammonia or deposited nitric acid, and some volatile organic compounds (VOCs) may react to make a variety of oxidised organic products. Furthermore, formation of nitrous acid (HONO) and formaldehyde in the gas phase has been reported. HONO is an irritant and will likely be detected as NO_2 in the AURN analysers (which use molybdenum catalysts). The atmospheric chemistry of HONO and formaldehyde will help promote VOC oxidation and will therefore likely lead to NO-to-NO_2 conversion and the generation of ozone. The experimental evidence available shows that the amount of HONO formed can be highly variable.
- Model simulations using the ADMS-Urban model for a London-wide paint application and within a street canyon suggest very small reductions in NO_x concentration up to about 0.7%. These results are uncertain however given the complexity of deposition processes in urban areas. Actual effects are likely to be smaller because it is unlikely that such large areas could be covered in photocatalytic paint.
- A 0.7% reduction in NO_x concentration could be achieved by a 1.1% reduction in road traffic NO_x emissions on the street based on a central London vehicle mix. These estimates, which are based on the NAEI and PCM model, should be considered as approximate given the uncertainties involved.
- To observe an impact on atmospheric concentrations due to catalytic surfaces the removal rate at the surface must be comparable to the emission flux.

- The efficacy and consequences of using photocatalytic paints for air pollution abatement purposes is challenging to evaluate compared with technologies that aim to reduce emissions at source. These challenges are focussed in two main areas. First, 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. Second, there is uncertainty in the composition of the reaction products arising from photocatalytic reactions – many of which potentially have important consequences for wider atmospheric chemistry.

Taken as a whole, there is little current evidence to suggest the widespread use of photocatalytic surfaces will reduce ambient concentrations of NO_2. Furthermore, there is a risk that these materials will result in the production of other undesirable species such as nitrous acid and formaldehyde, which can have wider impacts on atmospheric chemistry as well as adverse health impacts.

Photocatalytic surfaces can reduce concentrations close to the treated surface but this will not result in significant reductions in NO_2 concentrations in the surrounding air. It is not physically possible for large enough volumes of air to interact with the surface under normal atmospheric conditions and therefore this method will not remove sufficient molecules of NO_2 to have a significant impact on ambient concentrations.

- Whilst AQEG does not recommend further field trials any that are undertaken need to be comprehensive and conducted under realistic conditions. Such work would carefully consider issues related to experimental design to robustly quantify before/after changes to ambient concentrations to ensure that any changes in pollutant concentrations can be related to the TiO_2 surface and not to other factors.
- There is a need to measure a comprehensive suite of pollutants as part of field trials to better quantify some of the important reaction products that have wider consequences for urban atmospheric chemistry.
- More needs to be known about the potential deactivation of TiO_2 surfaces due to pollution loading and other environmental factors. This issue will affect the potential long term efficacy of the surfaces over time, perhaps leading to additional re-applications of TiO_2 paints.

Introduction and Context

1.1 What is photocatalytic paint?

Photocatalytic paint is paint that contains titanium dioxide (TiO_2) that acts as a catalyst when exposed to ultraviolet (UV) light, leading to the removal of atmospheric pollutants. Similar to other catalysts, the catalyst itself remains unchanged but promotes the conversion of a pollutant into other species. The paints are available from several commercial companies and marketed under different names.

While the photocatalytic paints have been the primary focus, these paints are part of a larger family of products that contain TiO_2 including paving, self-cleaning glass and roof tiles. TiO_2 can also be applied as a water-based spray containing nano-TiO_2, which cures to form a hard, transparent 40 nm thick surface. Additionally, clothing has been developed to incorporate catalytic properties with the aim of mitigating air pollution (Scientific American, 2012)

Most of the recent interest in photocatalytic paints is as abatement technology for nitrogen oxides (NO_x) but the reactions can involve other pollutants such as volatile organic compounds (VOCs). Furthermore, TiO_2 surfaces have also been tested to determine whether they reduce concentrations of other species such as ammonia and nitrous oxide from animal husbandries (Guarino et al., 2008). These surfaces work though photocatalysed oxidation of NO_x to surface-adsorbed nitrate, which is then washed off. The surface is superhydrophilic such that water forms in a film rather than droplets. Interest in these materials has increased in recent times due to the focus on reducing ambient NO_2 concentrations to meet EU Limit Values. Materials containing TiO_2 are used for three main purposes: the removal of certain pollutants from the atmosphere, self-cleaning surfaces and odour reduction. The focus of this report is on the ability (and consequences) of using these materials for air pollution abatement.

Photocatalysed oxidation is not specific to NO_x and it must be borne in mind that once surfaces are covered with highly reactive coatings, all sorts of things may react on them to make a potentially wide range of products.

1.2 Photocatalytic paint as a pollution abatement technology

The use of photocatalytic surfaces for pollution abatement is an attractive proposition in some respects. First, these are passive abatement technologies that only need sunlight to function. However, field trials have also been undertaken where ‘active’ artificial UV light sources have been used to illuminate surfaces. Second, they can be easily applied to a wide range of surfaces and are relatively cheap.

The vast majority of pollution abatement technologies for combustion products are concerned with abatement at source e.g. catalysts in road vehicles and electrostatic precipitators for stationary combustion. Photocatalytic surfaces fundamentally differ from most air pollution abatement technologies in that they do not aim to reduce emissions at source but aim to reduce concentrations once released to atmosphere. The latter point is very important because once released to the atmosphere it is much more difficult to remove pollutants simply because of the volume of the atmosphere compared to the surface area of any potential abatement technology e.g. through the reliance of interactions between surfaces and the atmosphere. A corollary of this is that the efficacy of photocatalytic paints depends on the pollutant flux to the surface (and associated destruction mechanisms) outweighing the flux into the atmosphere from the emission sources. This is explored further below.

The other important aspect of photocatalytic paints is their efficacy cannot be controlled or measured in the same way as the reduction of emissions at source. It is generally much easier to control and measure the efficacy of source emission reduction compared with ‘after the fact’ control. For this reason alone the choice of these materials as abatement technologies may not be as desirable as other source control technologies because the outcome is much less certain than that for source control. For this, and other reasons it can be challenging to robustly quantify their efficacy in reducing pollutant concentrations.

1.3 Perception of air pollution and building soiling

TiO_2 surfaces are extensively used for their self-cleaning properties on glass and other materials. Surfaces treated in TiO_2 can appear to be clean whether the material is glass or some other coated material e.g. buildings with white surfaces. These materials may help give the impression of ‘clean air’ because of their antifouling characteristics. These properties, while not directly related to the abatement of emissions are nevertheless a potentially important aspect of their use and wider air pollution perception. However, building cleaning (glass and building fabric) does have a real cost and the use of TiO_2 surfaces may help reduce the costs associated with building cleaning due to air pollution.

The self-cleaning properties of these surfaces are complex however and are related to several of their surface characteristics. First, the surfaces are superhydrophilic and effectively spread water droplets across the surface making it easier to wash off solid material. Second, any organic material coating on solid particles will react on these surfaces through photocatalytic reactions, leaving particulate that is much less ‘sticky’ than the original particle, allowing them to fall or wash off more readily. Third, it appears that many TiO_2 surfaces have very high electroconductivity e.g. Anandan et al. (2013). A surface with high electroconductivity provides anti-static properties – repelling charged particles and preventing their accumulation on the surface. The extent to which each of these processes is important is not well understood, and both the chemistry and physics of these surfaces is complex in nature.

Chemistry

1.4 Introduction

Titanium dioxide is a semiconductor material with a band gap of about 3.2 eV, which corresponds to the energy of near UV light with a wavelength of about 390 nm. Higher energy (shorter wavelength) light is therefore able to produce electron-hole pairs that can potentially initiate both oxidation and reduction reactions on the surface of the material. TiO_2 occurs naturally as the minerals anatase, rutile and brookite, which possess different crystalline structures and different photocatalytic activities (Chen et al., 2012). The activity of a particular sample or form of TiO_2 is therefore reported to depend on the contributions of these different minerals, and is also potentially influenced by the presence of other materials which may be included deliberately (i.e. doping) or as a result of ageing or soiling processes.

There has been considerable interest in the application of TiO_2 photocatalysis to air quality remediation, with particular focus on the removal of NO_x and volatile organic compounds (VOCs) from the atmosphere. In the former case, either NO or NO_2 are ideally oxidised to surface-bound nitrate, which is then removed by wash-off. In the latter case, a VOC (e.g. benzene) is ideally completely oxidised, leading to the release of CO_2 into the gas phase. As described further below, however, there is also the potential for the production of unwanted intermediate products, and the reactivity of the TiO_2 surface is not necessarily specific to the particular species of interest.

Once again, the reaction products are almost certainly influenced by the mineral composition of the TiO_2 material and the presence of other materials. It is therefore not straightforward to predict the impact or performance of a particular TiO_2-based product from existing information, such that each product ideally needs to be tested and characterised individually using standardised methods (e.g. as described by Ifang et al., 2014).

1.5 Studies of the rates of NO_x reactions on TiO_2 surfaces

The reactions of NO_x on TiO_2 surfaces have been studied in numerous laboratory investigations over the past few decades (e.g. Chen et al., 2012; and references therein), stimulated both from the potential applications of TiO_2 coatings in pollutant abatement, and also from interest in reactions occurring on mineral dust particles.

The rates of heterogeneous reactions are usually formally described in terms of a reactive uptake coefficient (γ), which is the probability that a molecule colliding with the surface of interest is actually taken up by reaction at that surface. This parameter therefore provides the basis for the rigorous kinetic representation of a heterogeneous reaction in modelling studies. Measurements of γ for the photosensitised reaction of NO_2 with TiO_2 surfaces have been reported in a number of studies (e.g. Gustaffson et al., 2006; Ndour et al., 2008; Monge et al., 2010a; Bedjanian et al., 2012), with these generally considering a mineral TiO2 composition of 80% anatase and 20% rutile. The results indicate that γ depends on conditions such as temperature, pressure, relative humidity, partial pressure of O_2 and the level of reagent NO_2. Monge et al. (2010a) have also shown that γ increases systematically with the proportion of TiO2 present in mixtures of TiO_2 with silicon dioxide (SiO_2). In addition, the removal of NO_2 has been demonstrated in a number of chamber studies in which commercial TiO_2-containing products were tested, without formally quantifying values of γ (e.g. Langridge et al., 2009; Laufs et al., 2010).

There are apparently no reported measurements of γ for reactions of NO on any atmospherically relevant surface, although its photosensitised removal on TiO_2 surfaces has been demonstrated in a number of chamber and laboratory reactor studies without quantifying values of γ (e.g. Lim et al., 2001; Monge et al., 2010b). Where direct comparison is possible, the results of chamber studies suggest that photosensitised uptake of NO and NO_2 occurs at broadly similar rates (e.g. Laufs et al., 2010), although their relative reaction efficiencies have not been studied extensively.

1.6 Studies of the products of NO_x reactions on TiO_2 surfaces

The majority of studies in which reaction products have been characterised have been carried out for the reaction of NO_2 on illuminated solid TiO_2 surfaces. These have included customised reactor glass surfaces coated with solid films of TiO_2 (Ndour et al., 2008; Beaumont et al., 2009; Monge et al., 2010a, 2010b; Bedjanian and El Zein, 2012), commercially-available "self-cleaning" TiO_2 coated window glass (Langridge et al., 2009), TiO_2 aerosols (Gustafsson et al., 2006) and powdered TiO_2-containing mineral dust (Ndour et al., 2008). These studies have all reported significant production of nitrous acid (HONO) in the gas phase, with a yield of about 50 – 70% (e.g. Langridge et al., 2009; Bedjanian and El Zein, 2012), with accompanying formation of hydrogen peroxide (H_2O_2) also observed (Beaumont et al., 2009). Other reported products include nitrous oxide (N_2O) and NO, formed in much lower yields (Bedjanian and El Zein, 2012).

There is much more limited information on the products of the photosensitised reaction of NO on TiO_2, although the chamber investigation of Monge et al. (2010b) reported significant production of both HONO and ozone. The production of ozone was interpreted in terms of photocatalysed conversion of adsorbed nitrate (NO_3^-) to form NO_3 radicals. Once released into the gas phase, very rapid photolysis of NO_3 radicals (on the time scale of a few seconds) results mainly in the formation of ozone and NO_2, such that partial conversion of NO to NO_2 also occurs.

Product information from experiments not performed using solid TiO_2 surfaces appears to be limited to the investigation of Laufs et al. (2010), who studied NO_x uptake on commercial TiO_2 doped facade paints, containing a few weight % of TiO_2. Unlike the solid TiO_2 surfaces, the paints are slightly alkaline (pH 8 to 8.5), which influences the pH of adsorbed surface water. Quantitative conversion of NO_x to adsorbed nitrate, NO_3^-, was observed, with neither HONO nor N_2O formed significantly as products. Traces of hydrogen peroxide, H_2O_2, were also observed. The difference in behaviour compared with TiO_2 coated surfaces discussed above was attributed to the alkalinity of the substrate, such that product nitrite (NO_2^-) remains in solution in surface water rather than being promptly released as HONO. NO_2^- then undergoes further photosensitised oxidation to form NO_3^-. Based on the results of the study of Laufs et al. (2010), therefore, some TiO_2 containing paints appear to offer NO_x-reduction properties, with a much lower propensity to form unwanted products.

1.7 Generation of other species and implications

As indicated above, the photosensitised reaction of NO_x on TiO_2 surfaces can produce a number of products that have implications for air quality. In addition to the well-established air quality pollutant ozone, these include HONO and H_2O_2.

The potentially significant formation of HONO has implications for air quality. In addition to being a respiratory irritant, the subsequent chemistry of HONO also adversely modifies the air composition. The main fate for HONO under the photosensitised conditions of its formation is photolysis (lifetime probably < 15 minutes), forming NO and hydroxyl (OH) radicals. Under urban conditions, OH initiates the NO_x-catalysed oxidation of VOCs, likely leading to several NO-to-NO_2 conversions, and the formation of oxidised organic products. Some organic products (e.g. formaldehyde, HCHO) may also photolyse to generate free radicals that promote additional NO-to-NO_2 conversion, while others may be sufficiently involatile to contribute to the organic component of particulate matter. The overall effect of this chemistry will therefore likely be net NO_2 formation, with this also promoting the formation of ozone.

H_2O_2 is a well-established photo-oxidant, which can transfer efficiently to cloud droplets. In aqueous solution, H_2O_2 is a strong oxidising agent that is particularly important in the conversion of sulphur dioxide (SO_2) to particulate sulphate.

1.8 Other reactions on TiO_2 surfaces

Many other atmospheric constituents also potentially undergo photosensitised reactions on TiO_2 surfaces (e.g. Chen et al., 2012, and references therein), although these are generally less well studied than the NO_x reactions.

There is reported evidence for the photosensitised production of NO_x (and HONO) on TiO_2 surfaces. As discussed above, there has been some characterisation of “renoxification” processes, in which NO_2 can be regenerated (in conjunction with ozone) from photosensitised reactions of surface-bound NO_3^- formed from NO_x uptake (Monge et al., 2010b). This also suggests that nitric acid (HNO_3) deposited onto TiO_2 surfaces can also be converted to NO_2 (and ozone), with evidence for this reported by Rosseler et al. (2013). The photosensitised oxidation of ammonia (NH_3) has also been shown to produce HONO (Kebede et al., 2013).

There has also been some interest in the application of TiO_2 photocatalysis to the removal of volatile organic compounds (VOCs) from the atmosphere. While essentially complete oxidation to CO_2 and water has been reported (e.g. for a series of alkanes by Boulamanti et al., 2009), there are also a number of studies that suggest significant formation of oxidised intermediate organic products that are potentially detrimental for air quality (e.g. Auvinen and Wirtanen, 2008; Chen et al., 2012, and references therein), through acting as free radical precursors.

Evidence from field trials

There have been several field trials of photocatalytic paints under a range of conditions from actively lit spaces to applications in urban environments. Two EU-funded projects have also considered photocatalytic paints and these are summarised below.

EU PICADA (Photo-catalytic Innovative Coverings Applications for De-pollution Assessment) project considered among other things artificial street canyons with surface/volume ratios of 1 m^{-1} (typically street canyons have S/V <0.1 i.e. aspect ratio of <1). The measurements reported NO_x reductions of 40-80% (Maggos et al., 2008) but can be regarded as unrealistic due to the aspect ratio of the canyon (see PhotoPaq below). The PICADA project also considered an indoor car park coated in TiO_2 paint and illuminated with UV. Reductions of 19-20% NO and NO_2 were observed (Maggos et al., 2007). The car park was a 917 m^3 enclosed area with 322 m^2 surface (ceiling) painted. Illuminated by 20 UV bulbs and emissions from a single car. The study provides very little detail on the analysis.

Ballari and Brouwers (2013) considered the effectiveness of a ‘de-NO_x street’ based on measurements from a street paved with photocatalytic blocks (paving was 5 m wide and 150 m long). The blocks consisted of a 5 mm active TiO_2-containing layer. Comparisons were made with another section of street that had no TiO_2 coating. Vehicle flows were low (110 per hour on average). Measurements were made at three heights (5, 30 and 150 cm). A total of 26 sets of measurements were made on 26 separate days from February 2009 to July 2011 approximately over a period from 9am to 5pm using a commercial chemiluminescent analyser. The sample size is actually very small but the authors note the NO_x concentration was on average, 19% and 28% (considering only afternoons) lower than the obtained values in the control street. Under ‘ideal’ weather conditions (high radiation and low relative humidity) a NO_x concentration decrease of 45% could be observed. Ballari and Brouwers (2013) also note that the TiO_2 coating is not durable and would need to be re-applied many times to retain effectiveness.

Barratt el al (2012) assessed the impact of photocatalytic paint in a courtyard location in Camden where one wall was covered in photocatalytic paint. Used two chemiluminescent monitors 0.1 and 1.5 m from the wall. 16 months ‘baseline’ measurements followed by 9 month of measurements with painted wall and then ‘switched off’ for 5 months by covering the surface. Results were equivocal – while some changes in concentration were observed it was difficult to relate the changes to the timing of the paint application. There was more evidence of an increase in NO concentrations when the wall was covered up. The Barratt et al. (2012) measurements were based on chemiluminescent NO_x analysers with molybdenum catalysts, which would lead to potential interferences from nitrogen containing compounds such as HONO.

Most of the comprehensive recent work related to photocatalytic surfaces is associated with Photopaq (PHOTOcatalytic remediation Processes on Air Quality, EU-LIFE funded) project. The experiments that formed part of Photopaq were generally well-controlled and well-designed. The project aimed to evaluate the feasibility of using TiO_2 based products to alleviate the air pollution problem under real atmospheric conditions. The Photopaq project considered more realistic street canyons (with respect to aspect ratios) than PICADA and an illuminated road tunnel in Belgium.

Two experimental street canyons were considered (5m high, 5m wide and 50m long). The experiment was careful to consider the validity of the ‘control’ conditions i.e. ensuring the very close agreement of measured NO_x concentrations in the TiO_2-treated canyon and the control canyon without the TiO_2 coating. It was concluded that there was no difference between the active and reference street canyon NO_x concentrations when expressed as averages (active 7.32 ±0.30 ppb, reference 7.35 ±0.31 ppb). Although not considered in these studies, canyon shading will be important and also more northerly latitudes with less UV such as in the UK.

The tunnel measurements consisted of three approaches to quantify the effect of photocatalytic paint on concentrations of NO_x: an upwind-downwind comparison, before-after differences and lights on-off (Boonen et al, 2015). In all cases there was no evidence of a reduction in NO_x concentrations within experimental errors (Gallus et al, 2015). In addition, laboratory and modelling experiments using tunnel surface samples suggested a theoretical reduction of 0.4% in NO_x concentration. One useful characteristic of these experiments was the measurement of CO_2 as a tracer for road vehicle combustion, allowing the researchers to consider NO_x/CO_2 ratio changes. There were concerns about deactivation due to high pollution loading, which is a wider issue for these surfaces.

In both the tunnel and street canyon experiments significant amounts of formaldehyde (HCHO, a known human carcinogen) were formed. The formation was confirmed to occur through photochemistry. The formation was explained by the use of organic admixes in the applied TiO_2 material but also through the degradation of adsorbed VOCs.

In more recent work, Folli et al (2015) report the effectiveness of photocatalytic paving in Copenhagen. Folli et al (2015) carried out laboratory experiments and a field trial along a 200 m section of road with 100 m with photocatalytic paving. The authors claim "…the results of the field tests showed that under ideal weather and irradiation conditions, i.e. summer months, the monthly average NO concentration (based on day and night values) in proximity of the photocatalytic area was around 22% lower than the reference area." However, the analysis itself is not comprehensive and the reliability of analysis and its uncertainty is difficult to judge given the information available. For example, plots of UV irradiance against NO or NO_2 concentration show no obvious relationship. Furthermore, even if there was a relationship other confounding factors would need to be taken into account e.g. increased dilution through increased thermal turbulence.

Quantifying the efficacy of 'real world' studies are challenging because it is very difficult to set up a robust 'control' against which changes can be quantified. It can be difficult therefore to know whether observed changes are due to the intervention or natural/other variation. Many studies lack the detail required to judge whether the changes in concentration observed are due to TiO_2 or some other variation e.g. due to meteorological variation. Similarly, despite the potentially wide range of important reaction products from TiO_2 surfaces, many studies do not consider these aspects in sufficient detail.

Model simulations

Models provide an effective way of simulating the effects of photocatalytic paint at a range of scales. In particular it is possible to simulate the wider application of photocatalytic paints over a wide urban area and also model smaller scale effects e.g. within a street canyon. This section considers model simulations using the ADMS 5.0 model over a range of spatial scales and surface resistances. It should be stressed that deposition processes are complex and most experiments for species such as NO_2 have been based on deposition to flat, vegetated surfaces such as moorland. In urban areas the deposition processes are especially uncertain due to the increased complexity of dispersion processes e.g. increased turbulence due to buildings and other structures. The modelling has assumed that the surface resistance, r_s is 1000 s m^{-1} for 'base case' conditions (no photocatalytic paint) and a reduced value to 400 s m^{-1} in the case of photocatalytic paint use. There are very few measurements of surface resistances for NO_2 in urban areas in the literature. The values used here arose from discussions with Professor David Fowler. Note that the surface resistances are assumed to apply to NO, not just NO_2, and that the lower surface resistance for painted surfaces ought only to be applied to daylight hours and not all hours as assumed below. For these reasons the calculations are likely to overestimate average deposition fluxes.

Before considering the results from the detailed modelling it is worth exploring the orders of magnitude of the fluxes involved in the process. It is stressed that the analysis given here is approximate but gives a good sense of the magnitudes involved. The flux, F, of NO_2 to the surface can be written as

$$F = -v_d C$$

Where v_d is the deposition velocity and C is the concentration. We assume

$$V_d = 1/(R_a + R_b + R_s)$$

Where R_a and R_b are the atmospheric (or aerodynamic) and quasi-laminar resistances respectively and R_s is the surface resistance. Taking R_a = 12.4 s m^{-1} and R_b as 10.4 s m^{-1} (see Annex), then with R_s = 400 s m^{-1} and 1000 s m^{-1} with C as 35 $\mu g m^{-3}$ (a typical average NO_2 concentration across London), the fluxes are respectively 0.083 $\mu g\ m^{-2}\ s^{-1}$ and 0.034 $\mu g\ m^{-2}\ s^{-1}$.

An annual emission rate of NO_x in London is ~50.6 kT/yr from the 2010 LAEI. If we assume for simplicity that half of this is NO_2 (an oversimplification but since ambient levels of NO_2 are roughly half those of NO_x in London the approximation is justified in this context). This converts to 0.502 $\mu g\ m^{-2}\ s^{-1}$ so we can see that the deposition flux in both 'paint' and 'no paint' cases is approaching an order of magnitude smaller than the emission flux[1]. On this basis one might expect the paint to have only a very small effect on ambient NO_2 concentrations.

1.9 Modelling NO_x paints in London

Figure 1 shows the modelled ground level concentration of NO_x in a transect from west to east for the uniform r_s cases with and without background NO_x concentration. The difference in concentration caused by a change across the whole domain of r_s from 1000 (no paint) to 400 s m^{-1} (paint) reaches a maximum of only 0.7 $\mu g\ m^{-3}$. The modelling shows that reducing the surface resistance through the use of photocatalytic paint makes very little difference to atmospheric concentrations of NO_x.

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[1] In practice two more fluxes will be important, namely the fluxes of NO_2 advected into and out of London and these along with the deposition and emission fluxes are discussed further in the Annex.

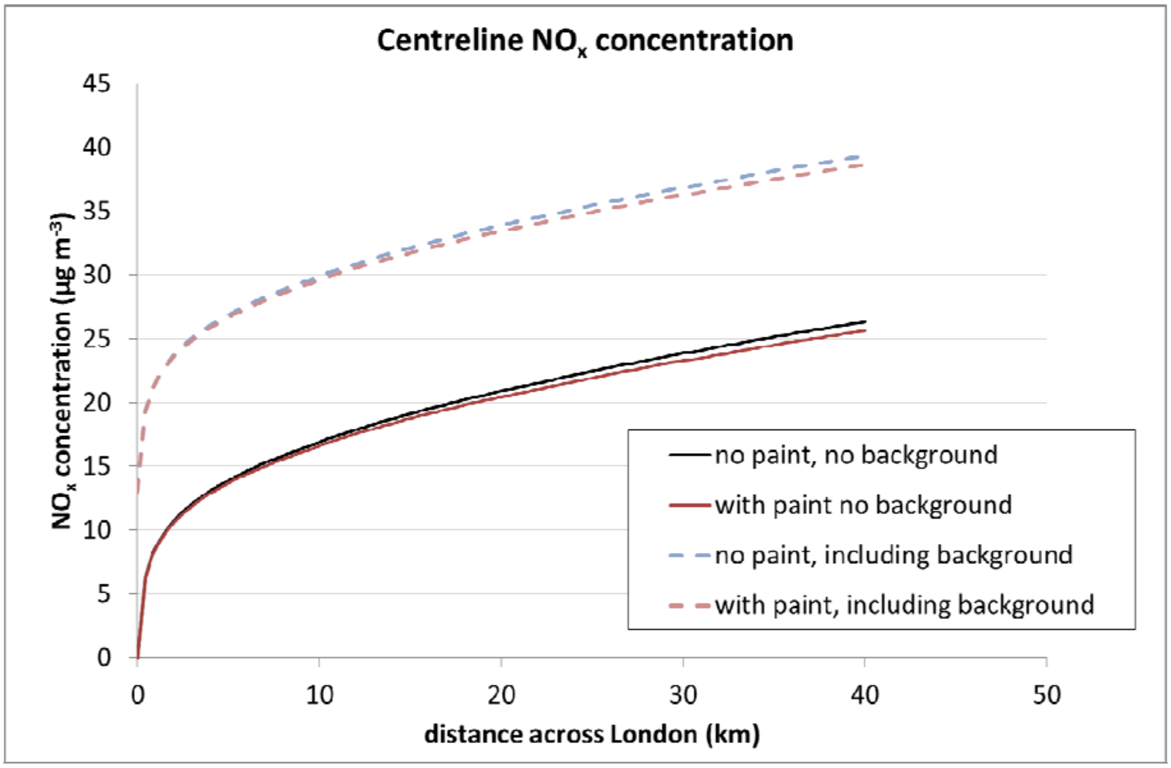

Figure 1 Modelled ground level concentration on an east west transect for uniform r_s

Figure 2 shows the impact of placing areas of paint (r_s=400 s m^{-1}) of differing size with the remainder of the domain having a surface resistance of 1000 s m^{-1}. Only the cases with no background NO$_x$ are shown. It can be seen that when the paint has a spatial extent of less than 1 km in the downwind direction that impacts on NO$_x$ concentrations are small.

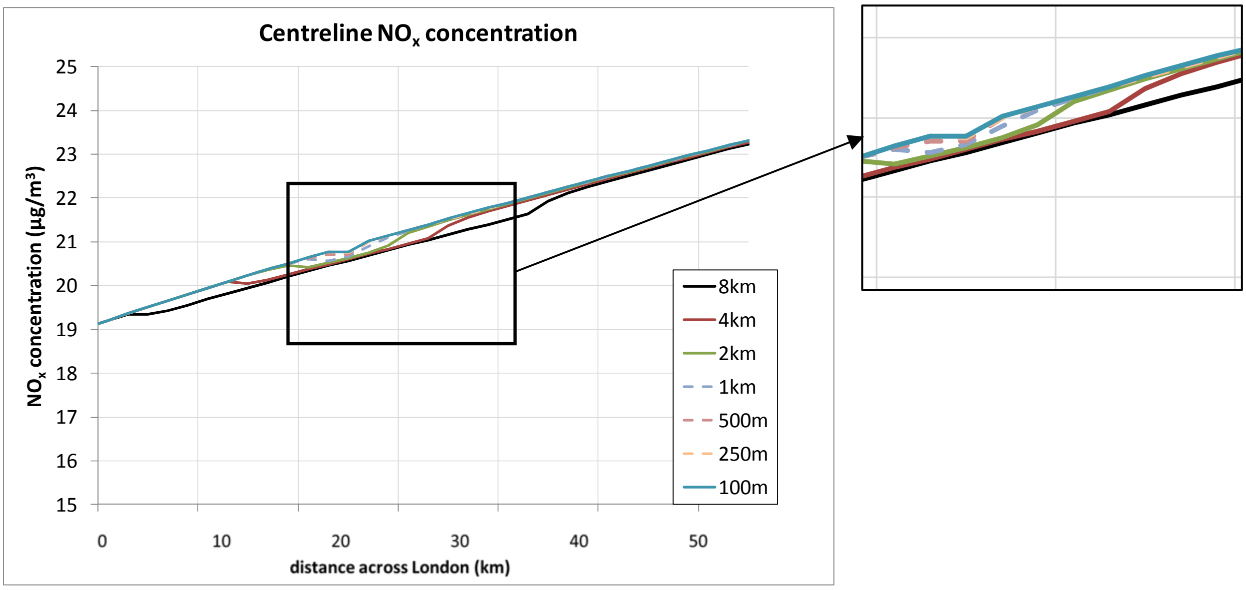

Figure 2 Modelled variation of ground level concentration on an east-west transect with the length of the area of reduced surface resistance (400 s m^{-1}) representing NO$_x$ paint. r_s =1000 s m^{-1} in the remainder of the model domain. In each case the area of reduced resistance is at the centre of the model domain. The key shows the length of the area of reduced resistance in each case. Only cases with no background are shown.

1.10 Simulation of effects in a street canyon

A single road in central London has been modelled using ADMS with an emission rate for NO_x, calculated from the 2008 LAEI traffic flows and speeds as 0.6 g km s^{-1}. No background or other emissions have been included. The impact of 'NO_x paint' for both a single meteorological case and for an annual average has been calculated. The annual average calculation used data from Heathrow Airport for the 2012.

The modelled domain is a transect across a busy central London street. Concentrations are only calculated within the street canyon.

Two runs were performed: one with Rs = 1000 s m^{-1} to represent the case when there is no 'NO_x paint', the other with Rs = 400s m^{-1} throughout the length of the street to represent NO_x paint with Rs = 1000 s m^{-1} everywhere else. In all cases the street was represented as a street canyon with height 17 m and width 20 m. As ADMS5 is not able to model the impact of street canyons and ADMS-Urban is not able to treat spatial variations in the deposition velocity, the two models have been used in combination to calculate the concentrations within the canyon taking account of deposition.

The model calculations for the single meteorological case and the annual average were calculated. The impact of the local reduction in R_s is seen to be very small, corresponding to a reduction in NO_x concentration of about 0.7%. To put this change in perspective, on a street canyon road in a busy city such as London, this reduction in NO_x concentrations could be achieved by reducing NO_x emissions from traffic on the street by around 1%. This could be achieved by reducing overall traffic flows on the street by 1% or by changing the fleet mix. A 1% reduction in NO_x emissions from a road characterised by the fleet mix in central London for example could be achieved by reducing the share of diesel cars in the car fleet on that road from 41% to 38%. It could also be achieved by upgrading 10% of all diesel cars, or 15% of all diesel vans in the fleet on that road to Euro 6 standards.

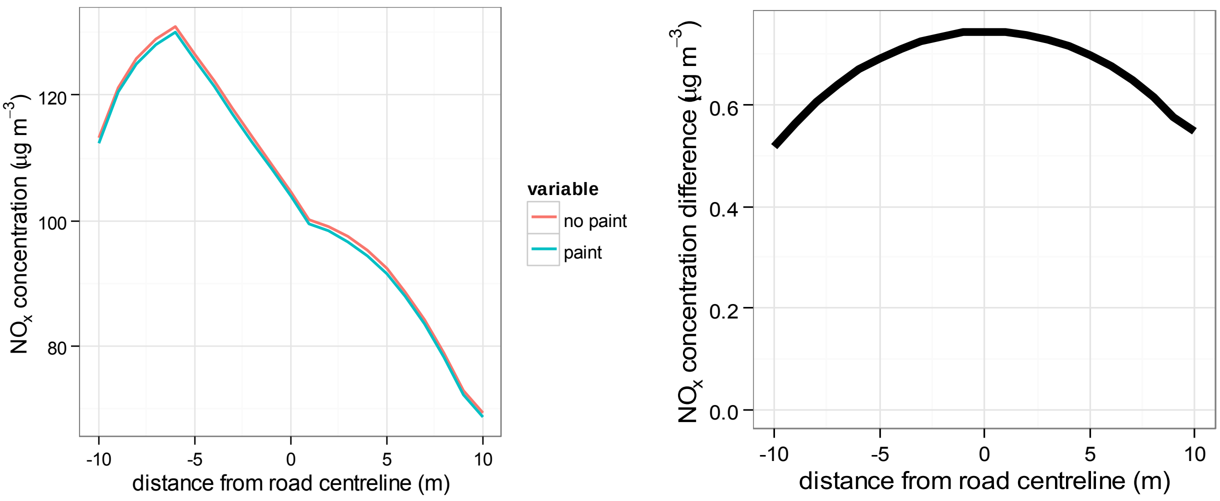

Figure 3 Left: Annual average concentration of NO_x on a transect across the street canyon showing the paint / no paint effects. Right: The difference in NO_x concentration between the paint / no paint case i.e. no paint minus paint concentration.

Conclusions

- There is increased interest in the use of outdoor photocatalytic surfaces as a means of reducing concentrations of various pollutants; principally NO_x and NO_2.
- There are many examples of materials that use titanium dioxide (TiO_2) to promote photocatalytic reactions including paint, concrete and glass.
- TiO_2 surfaces have been studied extensively in the laboratory and this helps to provide information on the chemical reactions that take place and the reaction products formed, although new information is constantly emerging. Under laboratory conditions photocatalytic surfaces have been shown to effectively reduce concentrations of NO_x.
- Compared with emissions source control, reducing emissions once diluted in the atmosphere is challenging. It is much more difficult to remove pollutants from the atmosphere because of the large volume of the atmosphere compared to the surface area of any potential abatement technology.
- There have been two large EU-funded projects considering these materials in the field: PICADA and Photopaq. The field trials from the former did report considerable reductions in NO_x concentration. However, the PICADA field trials were unrealistic in the sense that tests considered very high surface/volume ratios.
- The more comprehensive and carefully designed field trials carried out as part of Photopaq (street canyon + illuminated tunnel) provide no compelling evidence that these materials result in a reduction in NO or NO_2 concentrations.
- A field trial in London did not show strong evidence of reduced NO_x concentrations due to the photocatalytic surface and it was difficult to discern any clear effect that could be attributed to the influence of the paint.
- Other species are also known to undergo photosensitised reactions on TiO_2 surfaces, with possible consequences for air quality. For example NO_x may be generated from reactions of ammonia or deposited nitric acid, and some VOCs may react to make a variety of oxidised organic products. Furthermore, formation of nitrous acid (HONO) in the gas phase has been reported and formaldehyde. HONO is an irritant and will likely be detected as NO_2 in the AURN analysers (which use molybdenum catalysts). The atmospheric chemistry of HONO and formaldehyde will help promote VOC oxidation and will therefore likely lead to NO-to-NO_2 conversion and the generation of ozone. The experimental evidence available shows that the amount of HONO formed can be highly variable.
- Model simulations using the ADMS-Urban model for a London-wide paint application and within a street canyon suggest very small reductions in NO_x concentration up to about 0.7%. These results are uncertain however given the complexity of deposition processes in urban areas. Actual effects are likely to be smaller because it is unlikely that such large areas could be covered in photocatalytic paint.
- A 0.7% reduction in NO_x concentration could be achieved by a 1.1% reduction in road traffic NO_x emissions on the street based on a central London vehicle mix. These estimates, which are based on the NAEI and PCM model, should be considered as approximate given the uncertainties involved.
- To observe an impact on atmospheric concentrations due to catalytic surfaces the removal rate at the surface must be comparable to the emission flux.
- The efficacy and consequences of using photocatalytic paints for air pollution abatement purposes is challenging to evaluate compared with technologies that aim to reduce

emissions at source. These challenges are focussed in two main areas. First, 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. Second, there is uncertainty in the composition of the reaction products arising from photocatalytic reactions – many of which potentially have important consequences for wider atmospheric chemistry.

Taken as a whole, there is little current evidence to suggest the widespread use of photocatalytic surfaces will reduce ambient concentrations of NO_2. Furthermore, there is a risk that these materials will result in the production of other undesirable species such as nitrous acid and formaldehyde, which can have wider impacts on atmospheric chemistry as well as adverse health impacts.

Photocatalytic surfaces can reduce concentrations close to the treated surface but this will not result in significant reductions in NO_2 concentrations in the surrounding air. It is not physically possible for large enough volumes of air to interact with the surface under normal atmospheric conditions and therefore this method will not remove sufficient molecules of NO_2 to have a significant impact on ambient concentrations.

- Whilst AQEG does not recommend further field trials any that are undertaken need to be comprehensive and conducted under realistic conditions. Such work would carefully consider issues related to experimental design to robustly quantify before/after changes to ambient concentrations to ensure that any changes in pollutant concentrations can be related to the TiO_2 surface and not other factors.
- There is a need to measure a comprehensive suite of pollutants as part of field trials to better quantify some of the important reaction products that have wider consequences for urban atmospheric chemistry.
- More needs to be known about the potential deactivation of TiO_2 surfaces due to pollution loading and other environmental factors. This issue will affect the potential long term efficacy of the surfaces over time, perhaps leading to additional re-applications of TiO_2 paints.

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ANNEX SIMPLE BOX MODELLING OF PHOTOCATALYTIC PAINTS

This simple analysis explores the balance and competition between a deposition flux of NO_2 influenced by surface painting (removing NO_2) and the fluxes due to emission and advection into an area (adding to NO_2). The analysis takes no account of subsequent NO_2 chemistry following reactions at a painted surface.

The hypothesis is that in the three-component model of dry deposition, TiO_2 paint makes the surface resistance zero. So in

$$V_d = 1/(R_a + R_b + R_c)$$

R_c would go to zero if the surface were totally covered in paint which was completely effective at destroying every NO_2 molecule which reached the surface. V_d is the overall deposition velocity and R_a, R_b are the atmospheric (or aerodynamic) and quasi-laminar resistances respectively. We need first to quantify these terms. We will assume for simplicity a neutral boundary layer in an urban area such as London. In that case R_a is given by

$$Ra = (1/ku_*)\ln (z_{ref}/z_0)$$

With k=0.35, a reference height of 10m, and a 10m wind speed of $3.5ms^{-1}$, $u_* = ku(z)/\ln(z/z_0)$ and then $u_*= 0.532ms^{-1}$ and the aerodynamic resistance is

$$R_a = 12.4 \text{ s m}^{-1}$$

The quasi-laminar resistance is given by

$$R_b = (2/ku_*) (v/D_i)^{2/3}$$

Where v is the kinetic viscosity of air = $0.146 \text{ cm}^2 \text{ s}^{-1}$, D_i is the molecular diffusivity of the gas i (taken as $0.153 \text{ cm}^2 \text{ s}^{-1}$ for NO_2 from the documentation for the CMAQ model). This gives

$$R_b = 10.4 \text{ s m}^{-1}$$

The surface resistance term is more difficult to quantify accurately. There are very few measurements of this quantity for NO_2 in urban areas. We have used values of R_s of 400 s m^{-1} and 1000 s m^{-1} for 'painted' and 'non painted' surfaces respectively following discussions with Professor David Fowler.

The question then is, how important is dry deposition in influencing the ambient concentrations in a city like London, given a typical emission rate and wind speed?

We can use a simple box model to explore this. This is clearly a major simplification of the complex turbulent diffusion and deposition within an urban canopy like London, but it could illustrate some important features of the processes. This simple model balances the advected fluxes of a pollutant into and out of a box representing the city, together with the deposition flux and emission flux. In a square box of side a, with an emission rate Q (in mass per unit area per unit time), wind speed u, with the pollutant mixed up to a height h, the concentration C is given by the mass conservation equation:

$$\frac{dC}{dt} = \frac{u}{a}.(Cb - C) + \frac{1}{h}.(Q - VdC)$$

Where C_b is the background concentration advected into the box. We assume annual average conditions, so that if the box represents Greater London, a ~ 40 km, u ~ 3.5 m s^{-1}, QNO_x ~ 50.6 kt/yr (taken from the 2010 LAEI), and C_b = 13 µg m^{-3}, typical annual mean NO_x at Harwell and Lullington Heath. The plume mixing height is assumed to be 350 m, the value of the vertical dispersion parameter σ_z at half the box width (taken from R91 for Pasquill D stability with a z_0 of 1.0 m and an initial spread σ_{z0} taken to be 50 m).

To simplify the chemistry, given that roughly half the ambient NO_x is NO_2 (in volume terms) we assume that half the emission is NO_2 and that no other chemistry happens. This is rough and could be refined to make the emission fractions the same as the mass fraction in the ambient atmosphere. Integrating this equation first with a value of R_s = 1000 s m^{-1}, i.e. in a ‘no paint’ scenario, gives

$$C_{NO2} = 28.45\ \mu g\ m^{-3}$$

not an unreasonable value for an average across the whole of Greater London. If we assume R_s = 400 s m^{-1}, i.e. an approximation to a ‘fully painted ground surface’ scenario, the annual average NO_2 concentration becomes

$$C_{NO2} = 27.25\ \mu g\ m^{-3}$$

This suggests that even if the whole surface were painted then the change in concentration is likely to be small, in this model around 4.2%.