UNIVERSITY of York

Ricardo Energy & Environment

Catalytic Paints to Reduce NO_x

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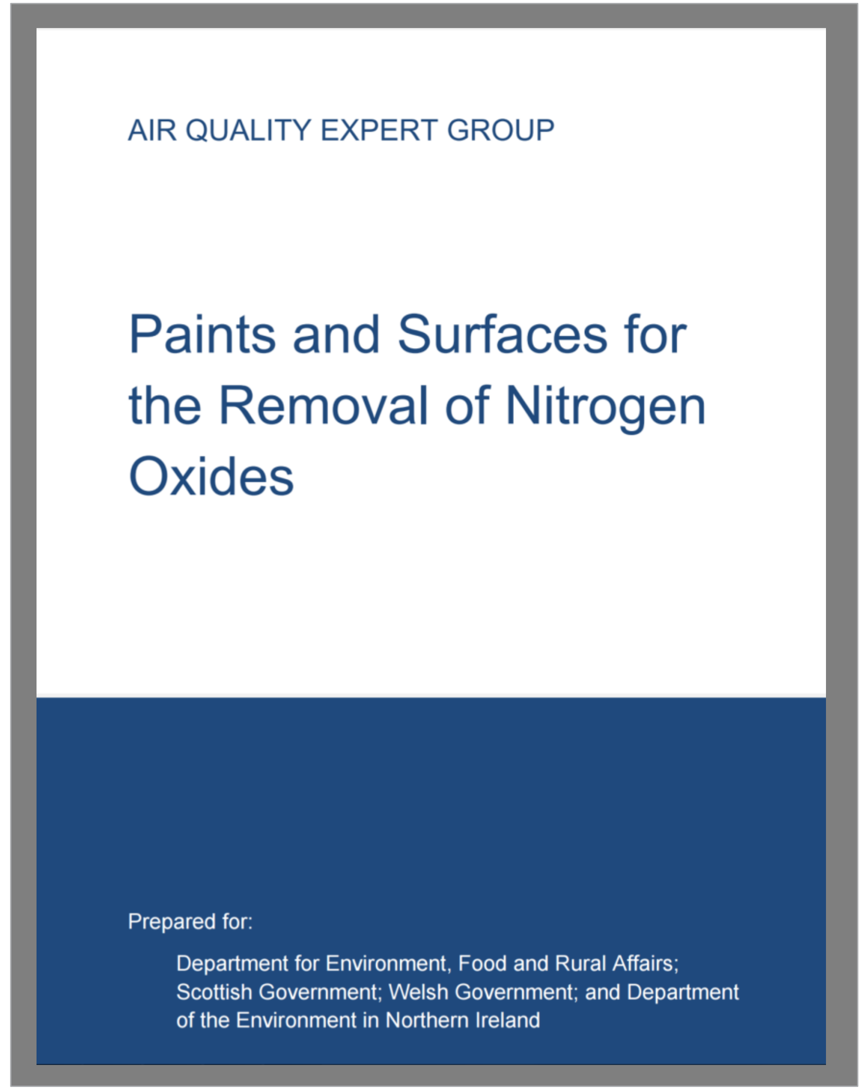
This talk

1. Will consider use of photocatalytic surfaces (*aka* ‘NO_x-eating paint’) as a means of reducing air pollution impacts
2. Cover some of the characteristics of this form of air pollution control
3. Think about the efficacy, field trials, evaluation and some important unintended consequences
4. Concluding remarks

AQEG report

- Published earlier this year
- First AQEG report to consider a specific abatement technology
- Interesting topic that consists of some of the most complex (and uncertain) aspects of atmospheric chemistry and physics
- Most of the presentation is based on the AQEG report



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

Photocatalysis

- In the presence of UV light, pollutants are removed on photocatalytic surfaces containing titanium dioxide (TiO_2)
- Known about since the 1920s
- Extensively studied in the laboratory
- Used in concrete surfaces, roof tiles, paving slabs, window glass, paints i.e. '*NO_X-eating paint*', sprays, …
- Aim is to convert potentially harmful pollutants to less harmful products e.g.
  - VOCs $\rightarrow$ CO_2
  - $NO_x \rightarrow HNO_3$/nitrate
- NO_x (NO_2) important for local air quality and NO_x + VOCs important for ozone formation
- **Potential to reduce concentrations of NO_2 in urban environments is particularly attractive at the current time**

Several attractive features

- **The potential to reduce air pollution!**
- Passive – no fuel or filters used to reduce air pollution
- Keeping buildings clean – public perception of air pollution
- Very easy to apply and 'cheap'
- Public engagement – this is a very important aspect of these materials
  - Public can be engaged in their use – photocatalytic 'poems'* and clothing!
  - Seems very benign / harmless
  - Easy to understand compared with the complexity of source emission control e.g. road vehicle after-treatment
- Several potentially important (and complex) characteristics
  - Surfaces are superhydrophilic (water droplets spread rapidly aiding wash-off)
  - Organic material on particles reacts with surface (photochemistry) leaving less 'sticky' particles that then fall off
  - Surfaces have high electroconductivity that provides anti-static properties – repelling charged particles and preventing their accumulation on the surface

*Simon Armitage In Praise of Air http://www.catalyticpoetry.org/#poem

Combustion vs. photocatalytic abatement of air pollution

- By far the most common approach to pollution abatement is the reduction of emissions at source
  - Catalytic converters on road vehicles, electrostatic precipitators for industrial applications etc.
  - These technologies can generally be well-controlled and are well-characterised
  - the outcome is usually well-understood and quantifiable
- Photocatalytic surfaces differ in important ways
  - They aim to reduce impacts ‘after the fact’ i.e. once an emission has been released to the atmosphere … after the entropy of the Universe has increased!
  - Has important implications for efficacy and *quantifying* efficacy
- ***How effective are these surfaces in reducing NO_x (NO_2)?***
- ***Potential to produce harmful intermediate species?***

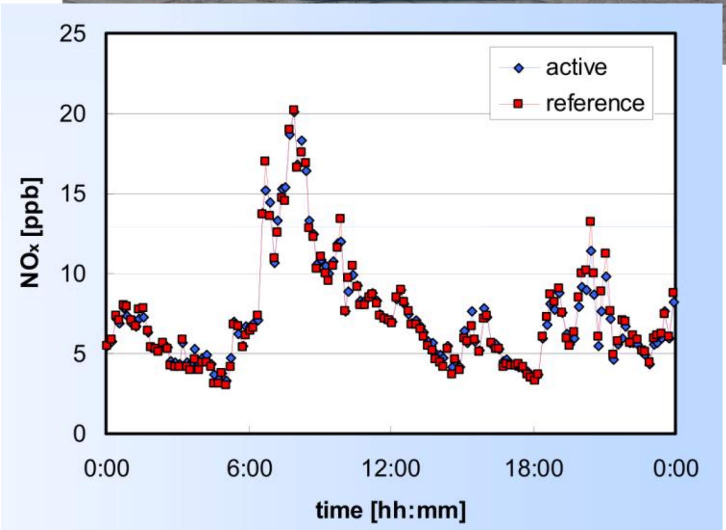
Street canyon controlled experiment

- EU LIFE PhotoPAQ (**PHOTO**catalytic remediation **P**rocesses on **A**ir **Q**uality) – arguably the most comprehensive assessment of these materials
- 5 x 5 x 50 m canyons, one 'active' the other not (reference)
- For NO_x:

  Active 7.32 ±0.30 ppb

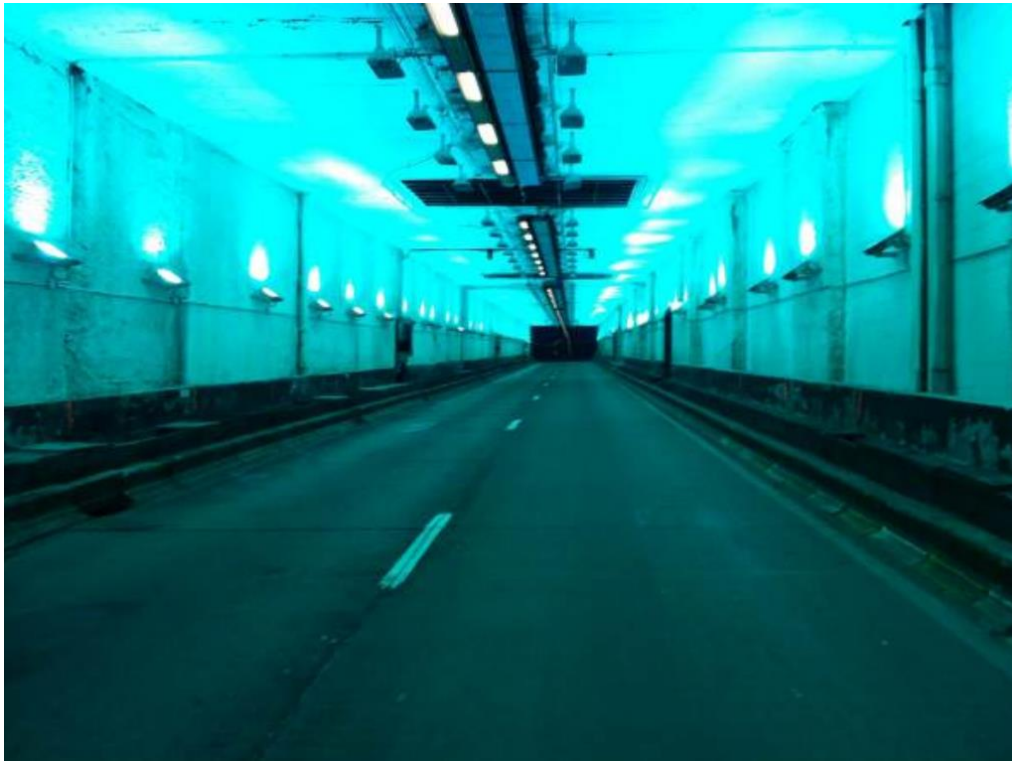
  Reference 7.35 ±0.31 ppb

No statistically significant evidence of a reduction in NO_x



Leopold II tunnel in Brussels*

- 160 m section treated
- Three approaches:
  - Upwind-downwind
  - Before-after
  - Lights on and lights off
- **No observable difference in NO_x concentration**
- Lab experiments suggest upper limit of 0.4% NO_x reduction
- Surface contamination (de-activation) important



*Gallus, et al., 2015. Photocatalytic de-pollution in the Leopold II tunnel in Brussels: NO_x abatement results. Build. Environ. 84, 125–133

The difficulty with evaluation

- There have been many evaluations and studies of photocatalytic materials in the laboratory
  - Under controlled conditions it is easier to quantify effects
- The robust evaluation of these materials in **real settings** is highly challenging
  - Tend to be set up as "before / after" experiments
  - The counterfactual i.e. what would have occurred if the surface had not been coated, is very difficult to determine
  - The effect of changes in meteorology over the before-after period can easily dominate the effects. This is rarely quantified and difficult to do anyway
  - The instruments used to measure differences probably are not measuring the right species
  - … a challenge for policy makers who would like some degree of certainty in the efficacy of different measures to control air pollution

Unintended consequences

- Surfaces have been shown to lead to the formation of nitrous acid (HONO), formaldehyde (HCHO) and hydrogen peroxide (H_2O_2)
  - Direct health effects, irritants, carcinogenic (HCHO)
- Atmospheric chemistry
  - HONO photolysed during daylight, forms NO + OH under urban conditions
  - OH initiates NO_x-catalysed oxidation of VOCs, likely leading to several NO-to-NO_2 conversions, and the formation of oxidised organic products
  - HCHO can also photolyse and lead to additional NO to NO_2 conversions
  - H_2O_2, strong oxidising agent, conversion of SO_2 to particulate sulphate
  - Overall effect is net NO_2 formation and increased formation of ozone
- Instruments
  - Chemiluminescent NO_x analysers with heated molybdenum catalysts will detect HONO as NO_2
  - Care needed when making field measurements…

Modelling surface deposition in urban areas

- Common model for deposition of gaseous species on surfaces uses the concept of surface resistances

$$r = r_a + r_b + \boldsymbol{r_s}$$

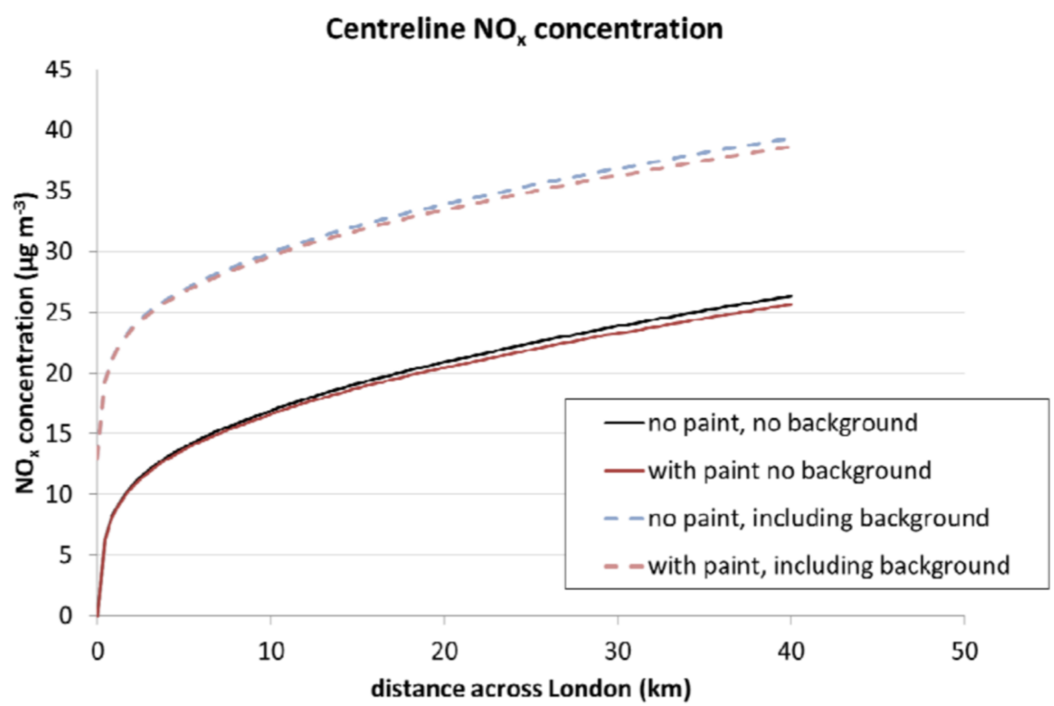
  - r_a is the *aerodynamic* resistance (controlled by atmospheric turbulence)
  - r_b is the *sub-layer* resistance (transfer across the final layer before surface)
  - $\boldsymbol{r_s}$ is the **surface resistance** that depends on the surface properties of a material (is zero for a perfectly absorbing material)
- Resistances, especially surface resistances, can be very uncertain – even more so in urban areas
- AQEG carried out modelling using a simple box model for London and ADMS for more sophisticated treatment of the processes

Modelling with CERC ADMS models

- ADMS 5.0/ADMS-Urban used to model simple scenarios in London
- Initial investigations at street canyon scale and whole London scale
- Model has been well-characterised for use in London, so a good place to start
- Estimated surface resistances used for NO_x based on discussions with Prof. David Fowler, CEH
  - 1000 s m^{-1} for base case (no photocatalytic paint)
  - 400 s m^{-1} for photocatalytic surface
  - Note uncertainties mentioned earlier

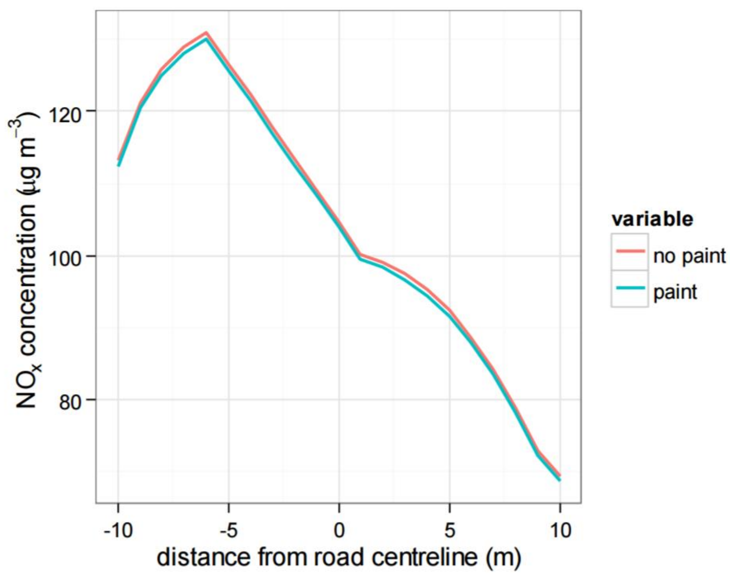
London-scale paint use

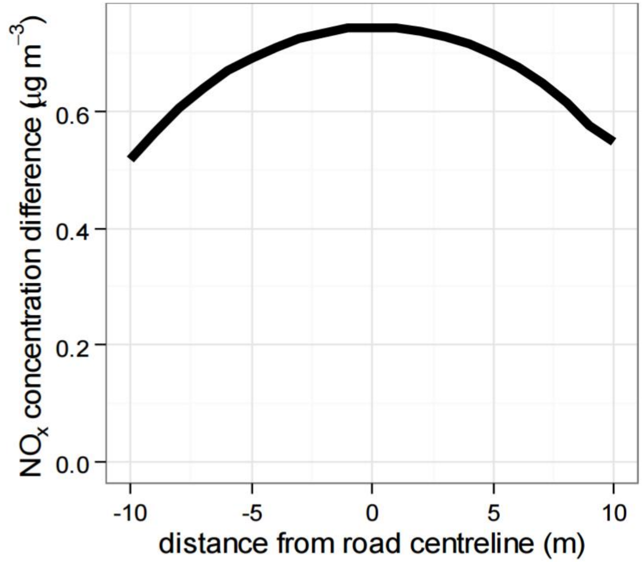
- Paint all of London in photocatalytic paint!
- Single meteorological condition, uniform emissions across London
- *Maximum* centreline concentration reduction was a 0.7 µg m^{-3} reduction in NO_x



Street canyon paint use

- Paint full length of a 'busy central London road' in photocatalytic paint (18 m high, 20 m wide)
- Full year of hourly meteorology
- Combined ADMS 5.0/ADMS-Urban approach
- Maximum predicted reduction is 0.7% in NO_x





Concluding remarks

- The AQEG report sums it up:

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.

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- The AQEG report sums it up:

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.

Thank you for your attention!

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