



# The Effectiveness of CristalACTiV™ for Depollution in Tunnels with Low Levels of Light

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**Abstract:** We have developed a new colloidal photocatalytic ultrafine titanium dioxide product (sol) which has been evaluated on a number of surfaces; including paint and concrete for depollution control in car parks and tunnels. The product is unique in particle size and crystallinity allowing it to be deployed in situations of low levels of light; less than  $1\text{W/m}^2$ . This product can be deployed at high concentration, whilst remaining invisible to the human eye. On concrete and painted surfaces, it has been proven to convert NO and NO<sub>2</sub> to harmless nitrate salts.

**Keywords:** photocatalysis; depollution; NO; NO<sub>2</sub>; nitrate; colloid; transparency; tunnels; low light levels; particle size; crystallite size.

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## 1. Introduction

The quality of the air in our living environment influences the quality of our life. Pollutants from motor vehicle exhaust or resulting from other types of combustion processes, harmful releases from chemicals used in our daily life or coming from industrial processes, are all potential sources of diseases and health problems. Photocatalytically treated surfaces can significantly reduce the concentration of those pollutants to safe levels, by converting them in harmless compounds.

Significant improvements have been made for the control of emissions from combustion processes, but more work is needed if we are to have cleaner air. Several environmental agencies and NGOs are raising the awareness of the health risks related to pollution. In previous years, the major focus has been on CO<sub>2</sub> and Particulate Matter (PM<sub>10</sub> and PM<sub>2.5</sub>); however, NO<sub>x</sub> levels in the atmosphere

continue to be a persistent contributor to the pollution problem and the levels are increasing in many major cities. Photocatalysis provides a way of converting harmful pollutants such as NO<sub>x</sub> and volatile organic chemicals into harmless materials.

Various studies have shown that actions implemented to control pollution, such as Low Emission Zones (LEZ) and the use of eco-friendly engines and cleaner fuels, have not provided the expected results and other technologies are required. Exposure to NO<sub>x</sub> causes multiple respiratory complications for the global population including airway inflammation in healthy people and increased respiratory symptoms in people with asthma. A recent study revealed<sup>1</sup> that more than 1,100 schools in London are within 150m distance from roads, carrying more than 10,000 vehicles a day. The same study showed that people living near roads carrying more than 10,000 vehicles a day are vulnerable to heart diseases and that air pollution could be responsible for 15 to 30% of all new cases of asthma in children.

The cost of damage caused by emissions in 2009, just from the industrial facilities reporting into the E-PRTR (European Pollutant Release and Transfer Register), is estimated as being at least EUR 102–169 billion<sup>2</sup>. Fifty per cent of the total damage cost occurs as a result of emissions from just 191 (or 2%) of the approximately 10,000 facilities that reported at least some data for releases to air in 2009. Three quarters of the total damage costs are caused by the emissions of 622 facilities, which comprise 6% of the total number.

Nitrogen dioxide (NO<sub>2</sub>) is a reactive gas that is mainly formed by oxidation of nitrogen monoxide (NO). High temperature combustion processes (e.g. those occurring in car engines and power plants) are major sources of nitrogen oxides, NO<sub>x</sub>, the term used to describe the sum of NO and NO<sub>2</sub>. NO makes up the majority of NO<sub>x</sub> emissions. A small part is directly emitted as NO<sub>2</sub>, typically 5–10% for most combustion sources, with the exception of diesel vehicles. There are clear indications that for traffic emissions, the direct NO<sub>2</sub> component is increasing significantly due to increased penetration of diesel vehicles, especially newer diesel vehicles (Euro 4 and 5). Such vehicles can emit up to 50% of their NO<sub>x</sub> as NO<sub>2</sub> (e.g. Grice et al., 2009<sup>3</sup>) because their exhaust after treatment systems increase the direct NO<sub>2</sub> emissions.

The trends in concentrations are linked to changes in emission sources. EU emissions of NO<sub>x</sub> fell 44% in the period 1990–2009 and 8% from 2008 to 2009. Nevertheless, total NO<sub>x</sub> emissions in 2009 were about 12% higher than the aggregated emissions ceiling set in the NEC (National Emissions Ceilings) Directive for 2010. Transport is the dominant sector for NO<sub>x</sub> emissions, accounting for 49% of the total in 2009, followed by the energy sector, which contributed 20% of the total<sup>4</sup>. These two sectors have substantially reduced emissions since 1990. Actual emissions from vehicles (often termed ‘real world emissions’) may exceed the allowed emissions specified in the Euro emission standards for each vehicle type. This is particularly the case for NO<sub>x</sub> emissions from light-duty diesel vehicles. EU Member States regularly update the emission factors used in their emission inventories and their previously reported emissions.

Directive 2008/50/EC states NO<sub>2</sub> limit values: Hourly value of 200ug/m<sup>3</sup> is not to be exceeded more than 18 times per calendar year. Annual limit value is 40 ug/m<sup>3</sup>.

## 2. Experimental Section

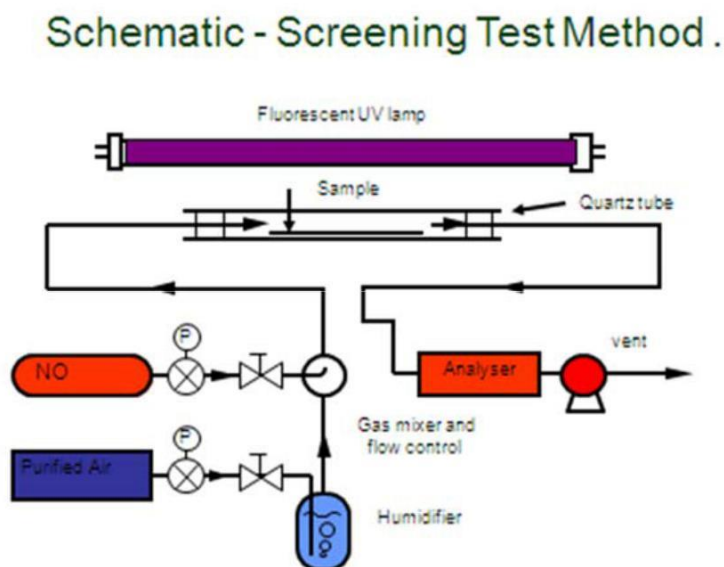
### 2.1 Preparation of nanoparticles

The raw material needed is metatitanic acid, which is then neutralized, washed and dried to form  $\text{TiO}_2$ . From here it is then pH adjusted using ammonium hydroxide and washed to remove any free sulphate. This product is then stabilized and peptised using proprietary Cristal technology, colloidal titanium dioxide sols - Fu, Monk<sup>5,6</sup>. The sol has a primary crystallite size of around 5nm when measured by Malvern; the product is commercially available as CristalACTiV™ PCS-7 sol with a concentration of 10%  $\text{TiO}_2$ , which is clear on application to surfaces at  $10\text{-}12\text{g.m}^2$ . The product is also available as KNOxOUT™ Clear from Pacific Paints.

### 2.2 Laboratory trial set-up

A tubular reactor and a standard CEN reactor were both used to demonstrate the effect of the coating on the removal of  $\text{NO}_x$  at various concentrations and levels of ultraviolet light. Various laboratory evaluations took place at both TNO –(Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek) and Cristal sites to determine the efficiency of the product and evaluate any possible reactions that could take place. As the European Community directive (2008/50/EC) is used to monitor  $\text{NO}_x$  levels in the environment, a chemiluminescence monitor was used with a test protocol similar to the ISO  $\text{NO}_x$  test (see Figure 1). The test sample measured  $18\text{cm}^2$  and was tested under the following conditions; 225ppb  $\text{NO}$  or  $\text{NO}_2$  at a flow rate of  $0.6\text{L/min}$ , 50% relative humidity and UVA light source giving equivalent to  $10\text{W/m}^2$ .

Figure 1.



### 2.3 Konningstunnel trial set up

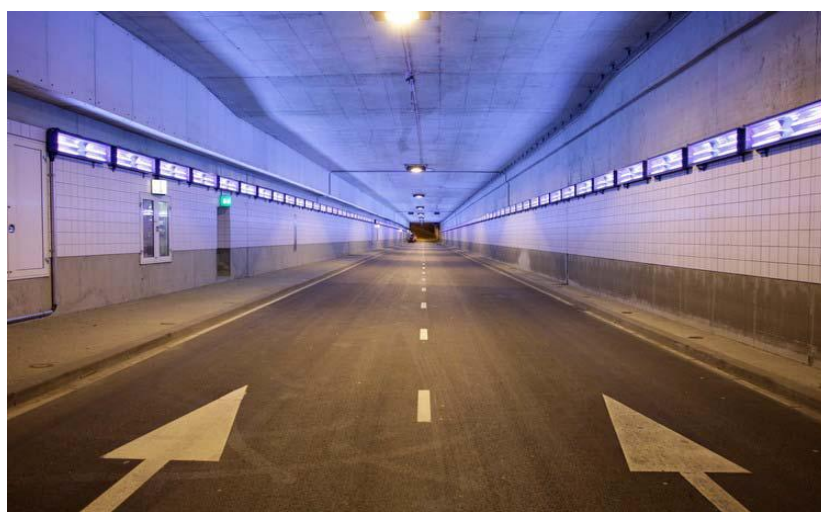
The need to mitigate pollution and help major cities achieve EU regulations is becoming increasingly more important. They have realised that it in order to avoid heavy fines that it cannot be done with one

single act or technology, but a combination. Many public areas are exposed to pollution and ultimately this leads to illness and premature death; all at high costs to the health sector. So, in order to help these initiatives several trials have been set up around the world in cities, schools, car parks and tunnels to demonstrate the benefits of applying photocatalytic products. For us, the tunnel of interest was located near a residential area, so pollution was a problem for people living in the area. In order to address the problem, several options were considered: 1) installation of a 4.5m high transparent screen covering the length of the residential area to prevent the pollution from the tunnel reaching the house area nearby; 2) diverting the traffic so that the amount of pollution in the area would be reduced, thus reducing the exposure to pollution for the residents in the area, or 3) application of innovative technology such as photocatalysis. The decision was made to evaluate the use of new and innovative technology. A project team was set up which included representatives from Philippines paint maker Boysen Paints KNOxOUT™, Cristal, Philips Lighting, Heijmans and Everts. The experimental monitoring campaign was conducted by Netherlands Organisation for Applied and Scientific Research TNO.

The tunnel is 650m long with a side exit about 400m down the tunnel. The trial section measured approximately 150m and was situated in roughly the last 250m of the tunnel. Chemiluminescent measurement devices were placed at the beginning of the trial section and at the end. In addition to the chemiluminescent monitors, nitrate accumulation strips were added to monitor directly the build-up of nitrates over time in the tunnel. The application of Boysen Paints' KNOxOUT™ Clear was made directly onto the concrete walls and ceiling. The lights shown in Fig.2 were designed by Philips Lighting specifically for the trial. They designed low energy fluorescent tube lamps which targeted the delivery of 25 Watts of 365nm UV light. The lights were designed with an Edison screw fit base E27.

The installation was carried out in conjunction with Philips. Resulting UV light intensities of  $1 \text{ Wm}^{-2}$  (wall) and  $0.6 \text{ Wm}^{-2}$  (ceiling) were measured at the tunnel surfaces during the trial.

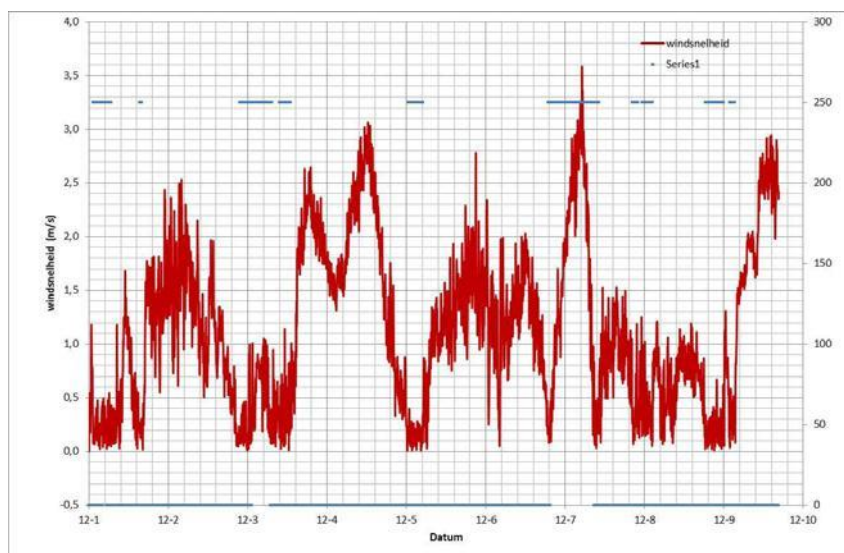
**Figure 2.**



Considerable time was taken to conduct wind tunnel and CFD modelling of the area outside and near the tunnel to understand the influences of wind flow, wind direction, pollution and other factors present. Background measurements were conducted for a short period of time before the application of the photocatalytic sol. These measurements provided information regarding the stability of the experimental

setup, and offered an opportunity to deal with issues proactively. Fig. 3 below shows a 10-day period of wind speed measurements in the tunnel. The graph shows the variability of wind speed, which depends both on weather conditions and on traffic flow.

**Figure 3.**



To demonstrate the photocatalytic effect within the tunnel, the concentrations of pollutants (NO<sub>x</sub>, NO<sub>2</sub> by difference, CO<sub>2</sub> and Ozone) were monitored at both the beginning and end of the treated test section. In addition, temperature, humidity, and air speed/direction were monitored at five-minute intervals. Actual traffic vehicle counts were monitored using a traffic camera and were reported on an hourly basis.

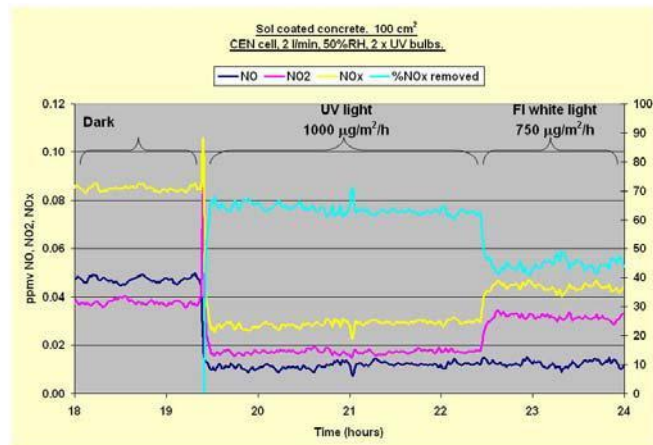
The UV lights in the tunnel were switched on and off at equal intervals to determine the photocatalytic effect. The period of the switching was adjusted to help reduce the effect of variations in tunnel conditions. A switching period of 24-hours was eventually selected, which matches some of the period behaviour of temperature, humidity, and both traffic density and air flow rates.

### 3 Results and Discussion

#### 3.1 Results and discussion (Laboratory demonstration).

During this work, it was agreed that the product was active to a good degree and it was shown to convert NO<sub>x</sub> to nitrate, with no increase in NO<sub>2</sub>, see figure 4.

**Figure 4.**



### 3.2 Results and discussion (Koningstunnel trial).

The average NO and NO<sub>2</sub> concentrations reported to be leaving the tunnel by the chemiluminescence monitors was 38 μg/m<sup>3</sup> and 34 μg/m<sup>3</sup> respectively. Statistical analysis of the results from the tunnel trial indicated a significant reduction in the NO but very inconsistent results on the NO<sub>2</sub> results, depending on the data subset that was analysed.

There are several studies that clearly state that chemiluminescence monitors should not be used to measure NO<sub>2</sub> in polluted areas, due to the identification of other nitrogen compounds as NO<sub>2</sub><sup>8,9</sup> Therefore, we decided that an alternative method of measuring NO and NO<sub>2</sub> would be employed. We know from the lab studies that NO and NO<sub>2</sub> react on the surface to form nitrates. Therefore we measured the accumulation of nitrate reaction products on sample strips placed in the tunnel. The source of the nitrate could only come from the reaction of the photocatalyst with NO<sub>x</sub>. These results are sometimes referred to as NO<sub>y</sub> measures, because they measure materials in addition to the NO<sub>x</sub> level (total of NO and NO<sub>2</sub>).

We prepared a mathematical simulation of the tunnel to estimate the amount of NO reduction that could be achieved. Our model indicated that the maximum removal of NO would be between 10% and 55%, depending on the air flow rate in the tunnel and the concentration of NO. These results compare well with the average reduction in NO measured by the chemiluminescence monitor of about 20%.

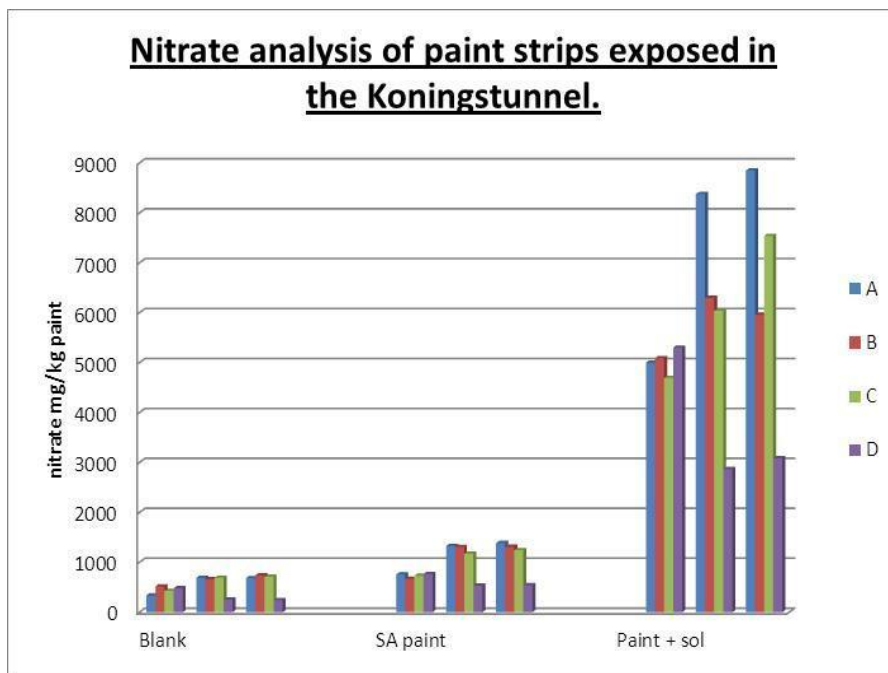
Several paints were drawn down onto melinex strips and the CristalACTiV™ sol applied to the surface. These were then positioned in four areas of the tunnel. They were put in the entrance and exit, both high and low to assess if the pollution changed at those locations (Fig 5). The fact that the sol was applied to paint, means that any nitric acid that has been produced is then neutralised by the calcium carbonate present in the paint producing calcium nitrate, which can be detected by washing out the calcium nitrate and measuring nitrate in the lab using Inductively Coupled Plasma methodology ( ICP).

**Figure 5.**



Fig. 6. shows the results after six weeks exposure for the analysed paint strips from the tunnel. Here we see that the blank paint (paint without photocatalyst) is showing no production of nitrate, as expected. Looking at the photocatalytic paint (SA - Styrene Acrylic paint) we see a gradual build-up of nitrate, which again is what we would expect. Once we apply sol to the top of the styrene acrylic paint, it is quite evident that this is the most active product for reducing NO<sub>x</sub> to nitrate. A and B identify those samples exposed at the beginning of the trial section, C and D identify those exposed at the end of the trial section. A and C are positioned close to the ceiling, B and D are positioned 1m above the pavement. It is also evident that the samples exposed at the beginning of the tunnel close to the ceiling are working the most efficiently. The samples at the end of the tunnel close to the ceiling are also showing good activity. The samples that were positioned low down show a decrease in nitrate build-up and it is thought that this is due to the excess water that the traffic may have brought to the surface, thus washing it out of the surface.

**Figure 6.**



Towards the end of the trial, samples of concrete from the tunnel wall and ceiling were recovered and sent to the laboratory for study. Work has also started to analyse the actual coated samples from the tunnel using an NO<sub>2</sub> specific analyser, a cavity ring down spectrometer. LGR NO<sub>2</sub> analysers use cavity enhanced laser absorption spectroscopy to measure the mole fraction of nitrogen dioxide continuously

and directly in flowing air samples. The test was set up using the following conditions: gas flow  $2.8\text{ l m}^{-1}$ , 60% RH controlled outside the cell, and irradiance of  $10\text{ W m}^{-2}$ . Gas compositions were varied. When using single gas, the concentration was set to 70ppb for  $\text{NO}_2$ , or 60ppb for NO. When working with NO and  $\text{NO}_2$  together, the concentrations were set to 50ppb (NO) and 70ppb ( $\text{NO}_2$ ). All concrete samples were taken directly from the tunnel. Concrete sample sizes were all  $50\text{ cm}^2$ .

Based on the nitrate results in fig.6, we can expect paint plus sol to accumulate on average, 6g of nitrate per kg of paint plus sol deployed, assuming the sol is as effective on the concrete surface in the tunnel as it is on the painted surface in the tunnel. This is a good assumption based on laboratory testing of the samples. We can then calculate that if the walls and ceiling were coated with 2500kg of paint plus sol, we could expect to accumulate 15kg of nitrate in one month. Assuming the traffic in the tunnel is made up of 75:25 gasoline: diesel vehicles and assuming the average vehicle emission is 0.2g/km (based on Euro V emissions regulations), we can therefore calculate for a 650m tunnel coated with the specified products that we can mitigate the pollution from 115,000 vehicles per month. This is a substantial portion of the traffic passing through this tunnel.

**Figure 7.**

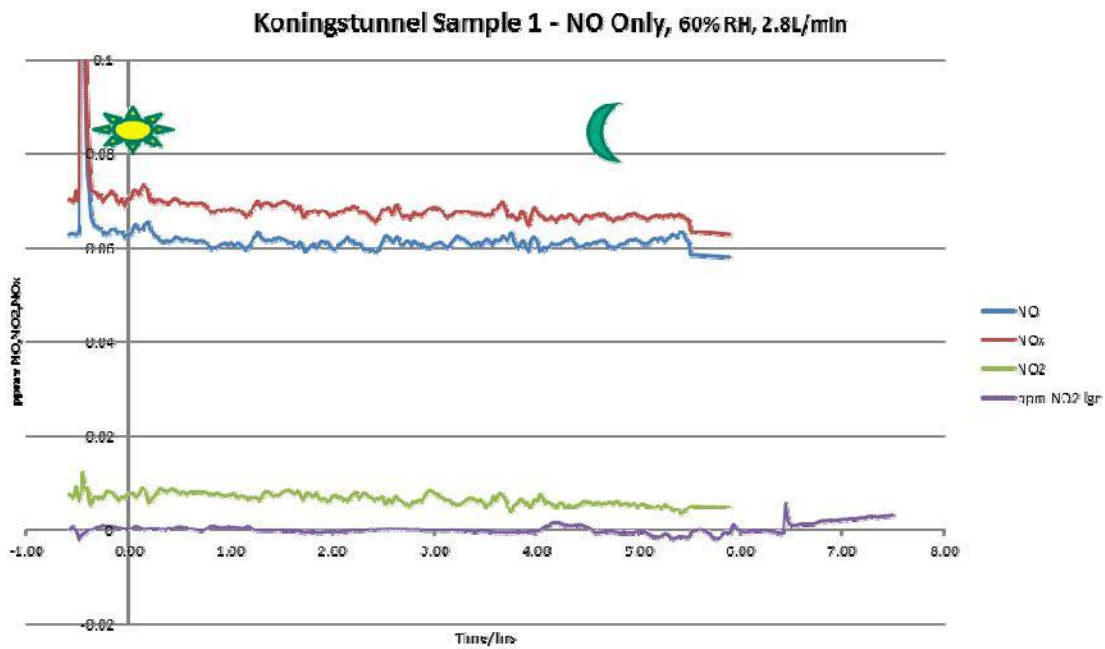




Figure 8.

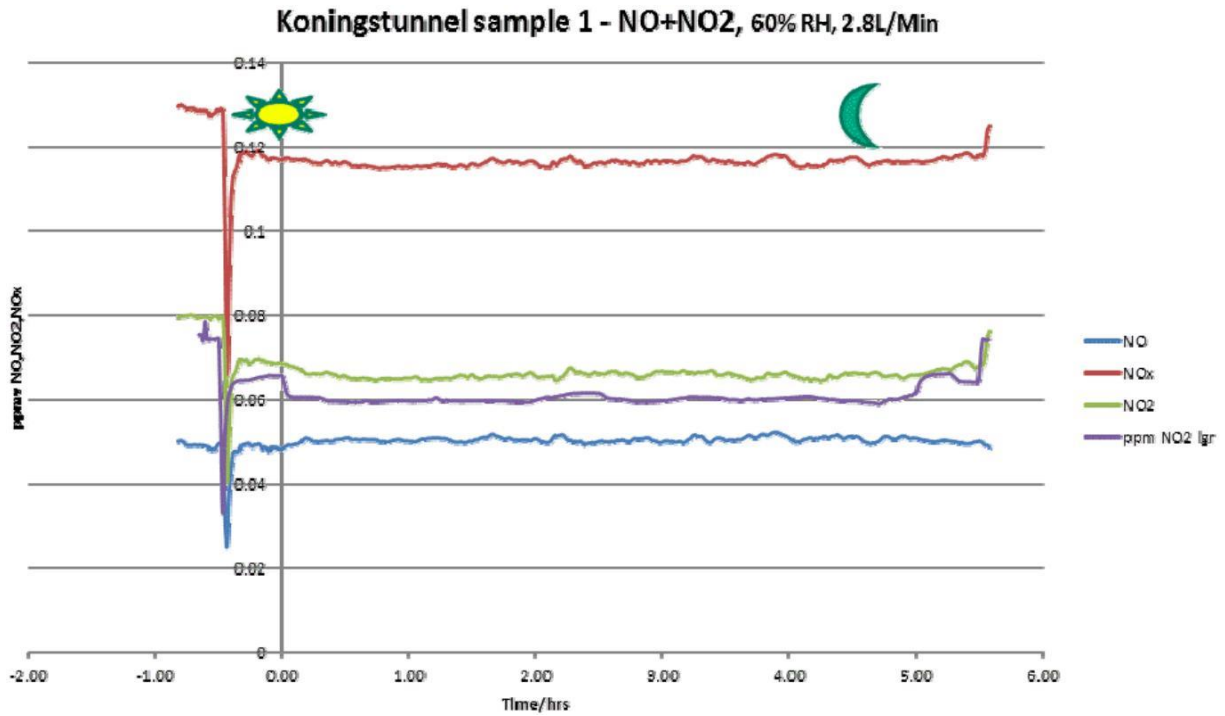
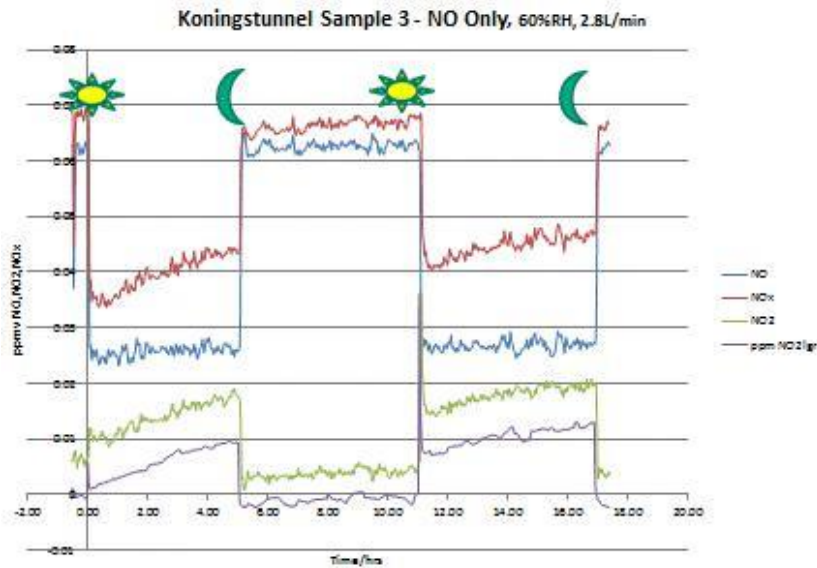


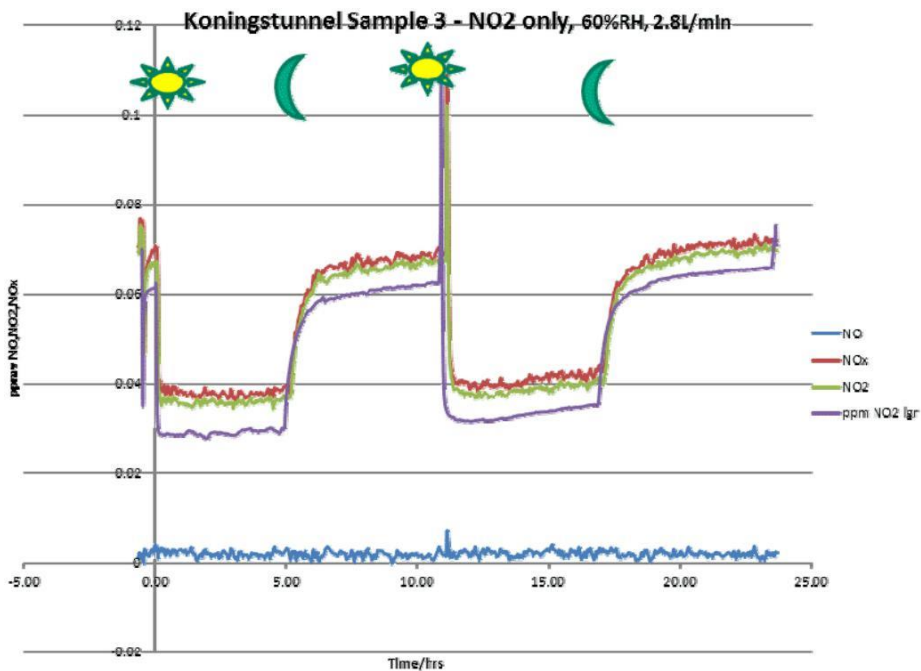
Fig 7 and 8 show the performance of untreated concrete samples extracted from the tunnel wall. The samples are tested under NO, NO<sub>2</sub> or a combination of both gases (NO and NO<sub>2</sub>). Fig. 9 shows the results for NO reduction when using a tunnel wall sample that had been treated with the sol. We can clearly see that the NO is converted to NO<sub>2</sub> first and then further converted to nitrate. The conversion to nitrate was confirmed by chemical analysis of treated and untreated test strips placed within the

tunnel during the final phases of the trial. Fig 10 shows that in the presence of only NO<sub>2</sub>, the NO<sub>2</sub> is converted further by oxidation to nitrate.

**Figure 9.**



**Figure 10.**



#### 4. Conclusions

From the results of the laboratory studies, as well as the field trial in the tunnel:

- We have learned that chemiluminescence monitors are useful to indicate if a level of NO<sub>x</sub> might exceed a certain level, but they are not useful to measure NO<sub>2</sub> levels, accurately, in polluted real-world environments. The reasons for the overestimation of NO<sub>2</sub> by these

analyzers is well documented, and is due to the presence of amines and other impurities present in the air<sup>7,8,9</sup>.

- We have shown that application of a photocatalytic sol can be effective in reducing NO pollution in a tunnel using artificial light. Given the intensity of the light used in the trial, one would expect the product to be even more effective on an exterior wall in the presence of sunlight.
- We have seen that under certain conditions NO forms NO<sub>2</sub> as an intermediate, and under laboratory conditions that it is always further oxidized to nitrate.

Increasing NO<sub>2</sub> levels in major cities is a problem. Since 2006, new diesel vehicles are being fitted with selective catalytic reduction converters to convert the NO<sub>x</sub> to nitrogen and water. The way they do that is to use urea (an amine) as a reductant. Therefore, since 2006, diesel trucks have been potential emitters of small amounts of amine through leakage. Gasoline stations all carry urea and are also possible emitters, so the background levels of amines has the possibility to be much higher than pre-2006. These amines will be recorded as NO<sub>2</sub> by chemiluminescence monitors as any amines are oxidized to NO<sub>2</sub> by the molybdenum catalyst in the monitor. Furthermore, in the Netherlands there are background levels of fertilizer and livestock waste products in the ambient atmosphere adding further to the possible amine levels which can bias chemiluminescence measurements. It is, therefore, critical to use other monitors such as the laser spectrometer suggested above to monitor NO<sub>2</sub> levels accurately.

We have seen from the Koningstunnel trial that we don't need high levels of UV light to activate the product. Although higher levels of light are beneficial, the product works well even at levels of 0.6 to 1 Wm<sup>-2</sup>. This product can be used in tunnels and car parks to reduce pollutants locally and avoid pushing them outside.

In conclusion, we have learned from the above trials the conditions under which KNO<sub>x</sub>Out™ Clear can be deployed to combat urban pollution and how it is possible to monitor the effects. The photocatalytic technology works best when pollution levels of NO<sub>x</sub> are high. When levels of pollution are low it is difficult to measure the effectiveness of this product, unless the surface area treated is large relative to the volumes of air entering the treated area and the lighting is adequate.

## **Acknowledgments**

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## Conflicts of Interest

The authors declare no conflict of interest.

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