Demonstration of Photocatalytic Remediation Processes on Air Quality

PhotoPaq’s Layman Report

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Introduction

Clean air is essential to people’s health and that of the environment. Since the industrial revolution, however, the quality of the air that people breathe has deteriorated considerably - mainly as a result of human activities. Rising industrial and energy production, the burning of fossil fuels and the dramatic rise in traffic all contribute to air pollution in our towns and cities which, in turn, can lead to serious health problems. For example, air pollution is increasingly being cited as the main cause of lung diseases such as asthma - twice as many people suffer from asthma today compared to 20 years ago.

The need to deliver cleaner air has been recognised for several decades with action having been taken at national and EU level and also through active participation in international conventions. EU action has focused on establishing minimum quality standards for ambient air and tackling the problems of acid rain and ground level ozone. Polluting emissions from large combustion plant and mobile sources have been reduced; fuel quality improved and environmental protection requirements integrated into the transport and energy sectors.

Despite significant improvements, serious air pollution problems still persist. Following its communication on the Clean Air For Europe programme (CAFE), the Commission has examined whether current legislation is sufficient to achieve the 6th EAP objectives by 2020. This analysis looked at future emissions and impacts on health and the environment and has used the best available scientific and health information. This analysis showed that significant negative impacts will persist even with an effective implementation of current legislation.

Among the new technical “solutions” designed for large dissemination over the public space, new photocatalytic building and coating materials are being widely proposed to stakeholders as well as public consumers.

In this project it was suggested to demonstrate the usefulness of photocatalytic materials for air pollution reduction in the urban environment.
What is photocatalysis?

In the very recent years, photo-catalytic self-cleaning and “de-polluting” materials have been suggested as a remediation technology mainly for NO\textsubscript{x} and aromatic VOCs in the polluted urban environment. The associated technologies have been launched on the European market with the aim to have a positive impact on urban air quality. These commercial products are based on the photo-catalytic properties of a thin layer of TiO\textsubscript{2} deposited at the surface of the material (such as glass, pavement, ...) or embedded in paints or concrete. The use of TiO\textsubscript{2} photocatalysts as an emerging air pollution control technology has been reported in many European areas. However, it seems that both the effectiveness and the real impact on air quality of these relatively new technologies up to now have been demonstrated only in a very limited manner before going into the European market.

Heterogeneous photocatalysis has been reported for gas and liquid phase remediation. Classically, the overall process can be decomposed into five independent steps:

1. transfer of the reactants in gas or liquid phase to the surface;
2. adsorption of at least one of the reactants;
3. reaction in the adsorbed phase;
4. desorption of the product(s);
5. removal of the products from the interface region.

While these steps are common to all heterogeneous processes (such as the uptake of a gas by a liquid droplet or heterogeneous catalysis), step 3 is where the photocatalytic nature of certain metal oxides plays a role. In fact, when a semiconductor catalyst (SC), such as a metal oxide (TiO\textsubscript{2}, ZnO, ZrO\textsubscript{2}, CeO\textsubscript{2},...), or sulfide (CdS, ZnS,...), is illuminated with photons carrying energy equal or in excess of its band gap, absorption of light promotes one electron into the conduction band, creating an electron-hole pair similar to photoinduced electron transfer. The oxide may transfer its electron to any adsorbed electron acceptor (thereby promoting its reduction), while the hole (or the electron vacancy) may accept an electron from an adsorbed donor (promoting its oxidation).
The work conducted so far has shown that the photocatalytic technology could reduce the concentrations of NO\textsubscript{x} and BTEX (benzene, toluene, ethylbenzene and xylenes) in air, although the absolute reduction potentials are still highly uncertain. However, the formation of other harmful species inferred from lab studies, such as HONO (known as a OH sources, facilitating ozone pollution, carcinogenic) and other oxidized hydrocarbons (aldehydes, PAN-type compounds, ...) as a result of the interaction between NO\textsubscript{x}/VOCs/particles and surfaces containing TiO\textsubscript{2} has not been assessed in atmospherically relevant conditions. The production of these later species may represent an important source of new pollutants in the urban environment and may have a strong impact on the oxidation capacity, radical concentrations and consequently on the building up of ozone pollution ("summer smog"). Accordingly, there is an urgent need for a better characterisation of such surfaces at atmospheric relevant conditions.

Assessing and demonstrating the effectiveness of these depolluting techniques have a real EU added value both in terms of policy making (and implementing the EU air quality strategy) and economics (by providing a demonstration of the actual performance of a new technique).

This project aimed therefore at evaluating the feasibility of using TiO\textsubscript{2} based products to alleviate the air pollution problem under real atmospheric conditions. This demonstration project is conducted independently i.e., it aims at testing existing technologies to asses if they work or not. Such a complete assessment and demonstration has not been performed so far (previous actions were always limited to some aspects (or pollutants) of the air quality issue.

The overall outcome of this project is an assessment of the potential of photocatalytic building materials and coatings for air pollution abatement.
Our goals

- Developing the testing methodology for photocatalytic removal/production of NO\textsubscript{x}, HONO, radicals, large type of VOCs and particles, with all tests being performed under atmospherically relevant conditions.

- Testing the photocatalytic activities of the commercially available TiO\textsubscript{2} based products in order to examine the pollutant removal effectiveness, (assessing if these depolluting surfaces are sinks or sources of pollutants).

- Designing better environmental indicators and methods to assess the impact of this new technology in European cities.

- Providing recommendation to the European authorities on the practical application for air treatment, (including a numerical "demonstration tool" for the depolluting action).
Preparatory actions

The performed laboratory measurements were important for both, the preparation, duration and strategic direction of the field measurement campaigns as well as to provide input data for the model calculations in the PhotoPAQ project.

The results of the laboratory reactors and chamber experiments indicated oxidation of several pollutants while others showed low or even no reactivity. Mechanistic and kinetic description of the reactions allowed estimation of potential atmospheric impact.

Different tools were used i.e., flow reactors and large scale simulation chambers.

The different samples were tested for their reactivity and product formation in the reaction of gas phase nitrogen species (NO\textsubscript{x}, NO\textsubscript{y}, e.g. nitrous acid, HONO), formaldehyde (HCHO) and selected volatile organic compounds (VOCs). In addition, possible re-noxification by photocatalytic reaction of adsorbed nitrate (NO\textsubscript{3}\textsuperscript{-}) was also studied. These experiments were performed as a function of several environmental parameters, such as relative humidity for which generally decreasing activity was observed with increasing humidity.

All samples, freshly prepared in the laboratory, were studied for their reactivity against nitrogen monoxide (NO). Reasonably high reactivities were observed for all samples showing the ability of the different tested materials to depollute air contaminated with NO\textsubscript{x}. Furthermore, it was demonstrated that the experimental conditions have a high impact on the degradation rates. It was found out that especially the pollutant concentration and the relative humidity are strongly influencing parameters. Atmospherically relevant low pollutant concentrations (below 50 ppb NO/NO\textsubscript{2}) and moderate relative humidities (RH 20-35%) resulted in the highest degradation rates.

The photocatalytic degradation of some VOCs was also studied, demonstrating a clear dependence of the reactivity of toluene, iso-pentane, 1-butane, α-pinene and benzene on the tested materials.
Demonstration in a tunnel

The first field site which has been chosen is an urban tunnel: the Leopold II tunnel. It is a bi-directional tunnel located at Brussels’ city centre, along the Basilica – Midi axis, within a densely built urban environment.

The geometry of the overall tunnel is highly complex, as it is about 2.5 km long and consists of two segments separated by a wall.

The tunnel is subject to a heavy traffic with a flow regularly reaching several thousands of vehicles per hour allowing us to have a sufficient level of pollutants. In spite of the complexity of the tunnel geometry, it was possible to identify a section of a length of 160m exhibiting a regular cross-section which enables a precise modelling of the air flow. It should be noted that as both tunnel tubes are separated in the chosen section by a wall, the used tunnel section can be considered as an one-directional tunnel.

Two heavily instrumented monitoring stations have been set up before and after the test section which was equipped with an additional UV lighting system. The first station – referred to as site 1 – is the first to be encountered by an air mass when the flow of cars induces sufficient air movements. At that station, the measurements are not considered to be affected by photocatalytic material effects in most of the time. The second one – referred to as site 2 – is generally fed with air which has been in contact with the photocatalytic materials.
Nitrogen oxides (NO\textsubscript{x})

The effect of the photocatalytic cement based coatings on the air remediation of NO\textsubscript{x} inside the tunnel test sections (70 and 160 m) was assessed by different means, using data of the NO\textsubscript{x}/CO\textsubscript{2} ratio from the two measurement sites, up- and downwind of the test section. Three different approaches were used to quantify the pollution reduction, i.e. measurements before/after application, upwind/downwind of the test section and with UV lamps on/off.

In contrast to first estimations based on laboratory studies on fresh samples, the field results show no observable reduction of NO\textsubscript{x} in the tunnel. An upper limit of 2 % was determined for the maximum possible NO\textsubscript{x} reduction, corresponding to the experimental uncertainties. As a main reason for the low remediation observed, serious passivation of the surface reactivity under the heavily polluted tunnel conditions was identified in laboratory experiments. Other reasons could be the high relative humidity, low temperatures, low level of irradiation and the wind speed inside the tunnel. A reduction of 10-15% can be calculated for the entire length of the tunnel.

Formaldehyde (HCHO)

Unexpected formation of small amounts HCHO was observed in the active test section. Higher concentrations were detected at the downwind site with the UV lamps on. In addition, the differences between the two sites were increasing with decreasing wind speed in the tunnel, which is explained by the variable dilution of the HCHO source.

Nitrous Acid (HONO)

During the tunnel campaigns no photocatalytic remediation of HONO could be observed during lamps on/off experiments, in agreement with the laboratory experiments.

Oxygenated volatile organic compounds (OVOC’s)

Concerning acetaldehyde, for the data analysis all measured acetaldehyde mixing ratios were plotted vs. CO\textsubscript{2}, no significant difference in the acetaldehyde/CO\textsubscript{2} ratio was observed for all periods. Thus, there was no evidence for a photocatalytic degradation of acetaldehyde based on the applied material and the artificial lighting system under the experimental conditions in this tunnel.
The choice of the outdoor field campaign site was the subject of many investigations and discussions. A field site in southern Europe (Petosino, Italy) was finally chosen. The field site is an industrial site located in Petosino – Sorisole few kilometers north of Bergamo. It is located on the side of a major road with an average traffic of ca. 8000 light vehicle and ca. 1500 heavy duty vehicles per day.

In this case, the demonstration strategy relied on the building of two identical areas on the field site delimited by walls.

Two artificial parallel street-canyons of 55 m long, 5 m wide and 5 m high were hence built equipped with sampling lines. After having checked the comparability of the two canyons, one has received the application of the photocatalytic coating while the other not. Two similar measurement stations were installed in both canyon and parallel measurements were carried out. The demonstration of the efficiency of the photocatalytic air cleaning was performed by comparing both sets of measurements.

The first ante-operam measurement was carried out from April 9th through to April 16th, data acquisition involved local pollution data such as concentrations of NO, NO₂, O₃, HONO, carbonyls, VOCs, CO₂, the sub-micron aerosol size distribution, chemical composition and mass and local weather parameters (temperature and relative humidity, wind direction and speed, spectral solar light flux). The outdoor campaign took place post-operam from April 9th to May 8th, 2013, involving more than 20 persons.
Nitrogen oxides

NO\textsubscript{x} concentration showed average differences between the active and the reference canyon of \(<2\%\) during daytime. However, in a conservative way and taking into account potential differences (instantaneous wind direction or NO\textsubscript{x} concentration) of the two canyons, a very conservative upper limit remediation of \(<10\%\) can be estimated. Both the actual observations (difference \(<2 \%\) assuming the expected similarity between the two sites) or the conservative upper limit (difference \(<10 \%\) including possible differences between the two streets) are much lower than results from other street canyon experiments. Therefore, realistic reductions will be only a few \%.

**Formaldehyde and acetaldehyde**

Concentrations were higher during daytime in the photo-catalytic active canyon. Acetaldehyde concentrations in both canyons are comparable in the ante-operam campaign confirming the expected general similarity of the two canyons. In contrast, higher concentrations were observed in the active canyon during daytime in the post-operam measurement. For formaldehyde similar concentrations are observed in both canyons during night-time, while at noon (with highest solar light intensity) higher concentrations were detected in the active canyon compared to the reference canyon. These emissions could be due to degradation of the small amount of organic components (\(<1\%)\) present in the cementitious mix, and/or to some VOCs adsorbed from the atmosphere and successively desorbed or transformed.

**Particles**

No significant difference between both canyons was observed in terms of: particle mass and size distribution, organic and elemental carbon, ions and organics adsorbed over the particles, particle number concentration; chemical composition.

**Ozone & VOC concentrations**

No significant differences have been detected, neither in the ante operam, nor in the post operam campaigns.
**Numerical simulations**

*Leopold II road tunnel campaigns in Brussels*

In order to assess the de-pollution efficiency two pollutants were assumed to be emitted inside the tunnel. One of them was assumed to be photocatalysed on the treated surfaces via the introduction of a sink in the transport equation. In this sense, numerical results reflect the upper limit of the expected reductions in the tunnel. In reality the deposition velocity inside the tunnel was much lower compared to lab scale tests, mainly as a result of the higher humidity, the heavily polluted tunnel conditions and the weaker than expected irradiance. Results for the expected reductions for the 70 m and 160 m sections and the entire tunnel are presented in the Table below.

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<th>Ventilation scenario</th>
<th>70 m</th>
<th>160 m</th>
<th>Entire tunnel</th>
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<tr>
<td>Ventilation OFF</td>
<td>2.0</td>
<td>2.5</td>
<td>15.1</td>
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*Outdoor field trial in Petosino, Bergamo*

The prevailing daylight meteorological conditions were identified and simulated. The de-polluting efficiency inside the street canyon was predicted a 15.2%, 4.4%, 5.2% and 7.1% for the E, S, SW and W wind directions.

*Assessment of the measured de-pollution*

Experimental findings lay in overall agreement with the numerical results in the sense that the estimated numerical de-pollution was in fact the upper limit that could be achieved. Similar conclusions were drawn for the case of the outdoor field campaign in Petosino, Bergamo.

*Cost benefit analysis*

The efficiency of this technology as an alternative means for the abatement of air pollution is highly dependent on the total costs at a local level and the potential monetary benefits in terms of reducing the external costs attributed to the adverse health effects of air pollution. As a result the efficiency of this type of technology differs among locations across Europe.
Conclusions & Outlooks

While the laboratory studies clearly demonstrate the effectiveness of the tested material for the degradation of NO\textsubscript{x} and potentially of some VOCs, the field testing revealed that the deployed conditions are critical for the expected pollution abatement. Within this project, two very different environments were tested, i.e. a heavily polluted tunnel in Brussels (Belgium) and an outdoor site in Petosino (Italy). Depending on the material tested, it was observed that heavy pollution could lead to a rapid passivation of the material. In addition, high relative humidity or emission of secondary pollutants (e.g. HCHO) could alter the depollution activities. Based on the experimental and modelling results of the present study it appears that reducing the air pollution by a few percent (i.e. ≤10\%) is a realistic target in typical urban environments which is limited - at least in part - by the transport of the pollutant to the active surfaces. In this context, however, it is important to note that just a few percent reduction of the NO\textsubscript{x} concentration is in range which can be expected from any applicable after-emission air quality improvement technology. Such abatements can however only be achieved with well formulated materials, exhibiting high depollution efficiencies and low passivation properties. Simple numerical tools have been developed to assess the required abatement efficiency and experimental conditions prior to any on site application.

Prior to any application, we recommend small-size experiments on possible deactivation of the photocatalytic activity under real atmospheric conditions. It is recommended to confirm high photocatalytic activity in real ambient air by using small scale flow reactor set-ups from the laboratory.