# Studies on photocatalytic active material using a new run off reactor (ROR) in the context of PhotoPAQ


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TROPOS Leibniz Institute for Tropospheric Research

Member of the Leibniz Leibniz Association

PHOTOPAQ Demonstration of Photocatalytic remediation Processes on Air Quality

Life

## Introduction and Project Presentation

Air pollution is a local, regional and transboundary problem caused by the emission of specific pollutants. Beside the most problematic pollutants particulate matter and ozone, nitrous oxides ($NO_x$) gained more and more importance. The major sources of $NO_x$ are high temperature combustion processes (e.g. from car engines and power plants). $NO_x$ have widespread environmental and health effects. They contribute to the acidification of soil and surface water and furthermore to the formation of ozone and particulate matter with associated climate effects. Nitrogen dioxide ($NO_2$) can affect the liver and lung and leads to an increased susceptibility to respiratory infection. Since 2010 the limit of the annual mean $NO_2$ concentration is 40 µg $m^{-3}$. Especially in urban areas car emissions at traffic hotspots lead to more frequent transgression of the $NO_2$ limit values. Therefore the interest in new methods to solve this problem is increasing. A promising idea in addition to reducing the direct emissions of the pollutants is the use of photocatalytic active materials. In order to do this, photocatalysts as titanium dioxide ($TiO_2$) were added to paints or concrete. Under irradiation with UV-light these materials are able to degrade air pollutants on its surface. The LIFE+ project PhotoPAQ (Demonstration of PHOTOcatalytic remediation Processes on Air Quality) wants to evaluate the feasibility of using such $TiO_2$ based photocatalytic active material to alleviate the air pollution problem under real atmospheric conditions. Before demonstrating the photocatalytic effect under realistic conditions it is necessary to identify reaction products for the photocatalytic heterogeneous reactions under laboratory conditions. In addition to established ISO standard reactors and to identify also low volatile photocatalytic reaction products in the aqueous run off of the coated model surface, a special reactor, called run off reactor (ROR), was developed at TROPOS. The data obtained will provide an overview on the behavior of nitrogen oxides and other air pollutants on these surfaces under irradiation with UV-light and allow an initial assessment of this material with respect to the goal of "improving urban air quality." This poster presentation will focus on the design of the new ROR and some first results.

### PhotoPAQ – Demonstration of PHOTOcatalytic remediation Processes on Air Quality

LIFE+ project January 2010 to December 2013
EU-project with the collaboration of 8 institutes
(France, Germany, Italy, Belgium and Greece)

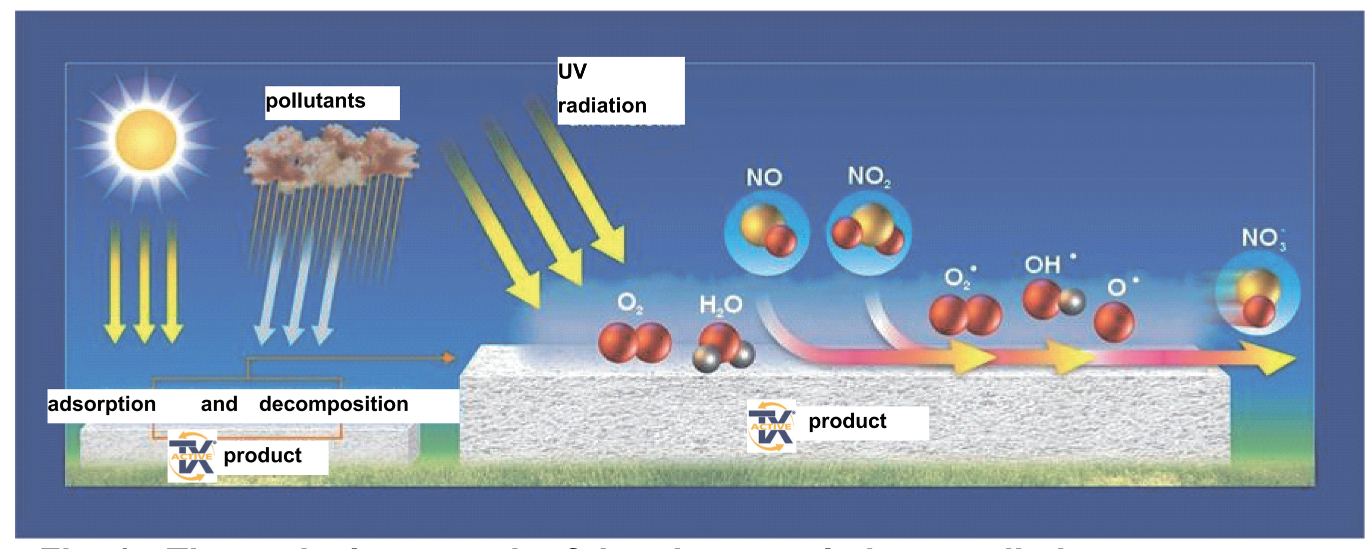



**Fig. 1: Theoretical approach of the photocatalytic remediation processes.** (source: Italcementi)

## Experimental Setup

### Scheme of the overall device and design of the new ROR

The new ROR is a small horizontal gas flow reactor, constructed almost as it is given in the ISO 22197-1: Test method for air-purification performance of semiconducting photocatalytic materials - Part 1: Removal of nitric oxide. The volume of the reactor is approximately 8.13E-03 $m^3$. To investigate the photocatalytic active concrete, the material is applied on sand blasted glass plates (dimensions 0.4x0.25m) with a thickness of 3-4 mm. The resulting volume to surface ratio is approximately 7.56E-02 m and therefore higher than in established standard iso-reactors. The uniqueness of the reactor are the additional rain bars. Up to 4 stainless steel tubes surrounded by teflon tubes can be installed to introduce water inside the reactor. The ROR enables us to extract the surface of the material after a test run without the necessity to open the complete system. This is an important advantage especially if experiments with hazardous compounds are performed. Furthermore it is possible, to simulate rain during an experiment and to identify the influence of the wetness of such surfaces, just by a small change of the ROR set up.

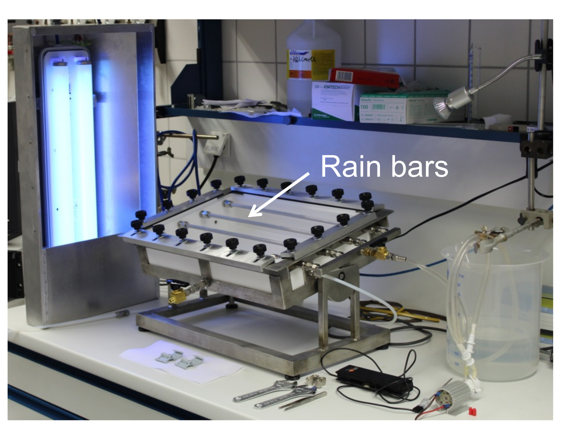



**Fig. 2: ROR**

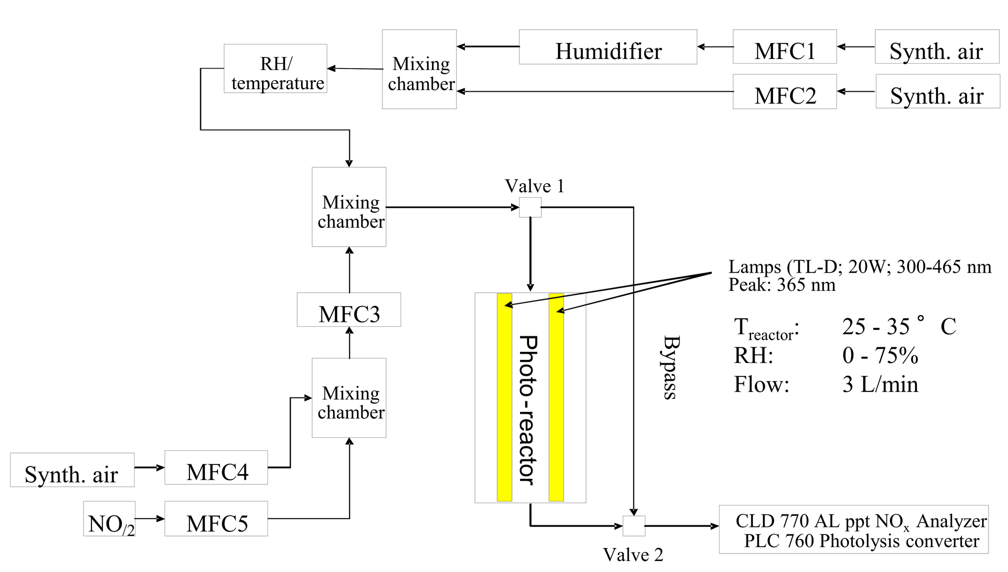



**Fig. 3: Scheme of the device**

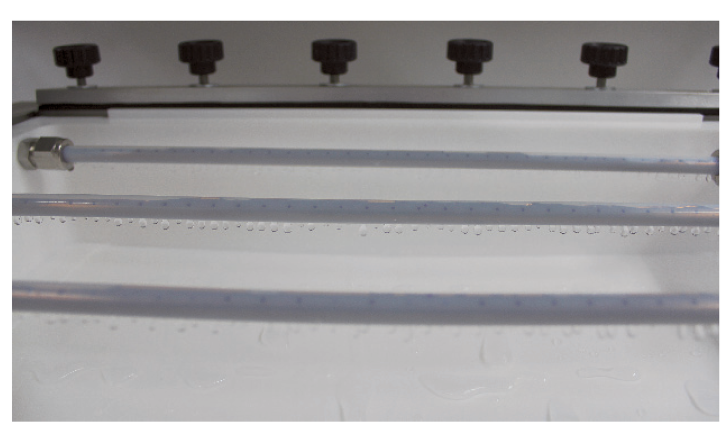


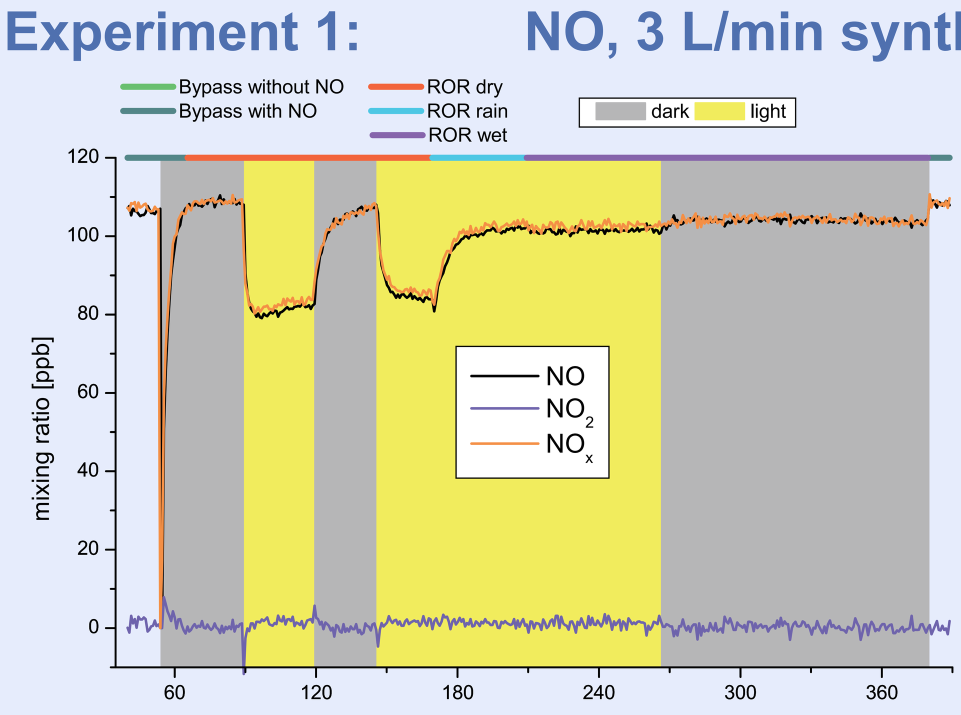
**Fig. 4: Simulation of rain inside the ROR**

### ROR operation procedure

1. Start experiment with pure synthetic air
2. Addition of the analyte
3. Adjustment of flow rate, mixing ratio and relative humidity
4. Measuring the bypass (no contact with the ROR)
5. Measuring under dark conditions
6. Switch on the UV-light
7. Switch back to Bypass
8. Extraction of the surface
9. Analysis of the aqueous extract

## First Results

### Experiment 1: NO, 3 L/min synth. air, RH50%



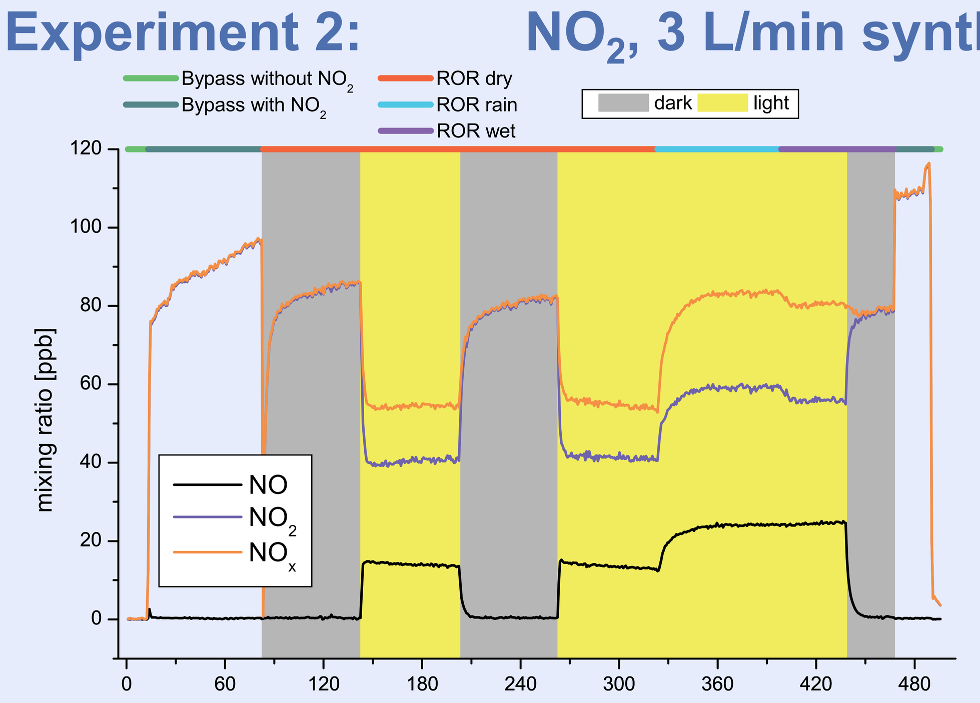

Bypass: $NO_x$ = 106.7 ppb
Dark / dry: $NO_x$ = 107.5 ppb
Light / dry: $NO_x$ = 84.2 ppb
reduction is about 21%

Light / rain: $NO_x$ = 102.9 ppb
reduction is about 4%

Light / wet: $NO_x$ = 102.6 ppb
reduction is about 4%

Dark / wet: $NO_x$ = 104.2 ppb
reduction is about 3%

### Experiment 2: $NO_2$, 3 L/min synth. air, RH50%




Bypass: $NO_x$ = 108.9 ppb
Dark / dry: $NO_x$ = 83.9 ppb
Light / dry: $NO_x$ = 44.7 ppb
reduction is about 59%

Light / rain: $NO_x$ = 83.1 ppb
reduction is about 24%

Light / wet: $NO_x$ = 80.4 ppb
reduction is about 26%

Dark / wet: $NO_x$ = 79.0 ppb
reduction is about 27%

### Discussion

The colour code on top of each graph describes the different working conditions. Both experiments start by measuring the bypass to determine the starting nitrogen oxides mixing ratios without any contact to the ROR. By switching a valve the gas streams via the ROR, first under dark conditions (grey). Nitrogen monoxide (Exp. 1) shows no dark reaction, meanwhile for nitrogen dioxide (Exp. 2) it can clearly be seen that there is a reaction even without light ($2NO_2 + H_2O \Longleftrightarrow HNO_2 + HNO_3$). After switching on the UV-light, both experiments prove the photocatalytic activity of the material indicated by the decrease of the $NO_x$ values (orange). Under these conditions the overall $NO_x$ reduction is approx. 21% for Exp.1 and up to 59% for Exp. 2. The subsequent dark and light period show the very good reproducibility of the results. The light blue colour on top of the graphs indicate the change in the working conditions. Additionally to light on, it started to rain, that means water drops continuously on the surface of the material via the rain bars. Consequently the $NO_x$ values for Exp. 2 increase almost up to the values under dark and dry conditions. Only for Exp. 1 remains a $NO_x$ reduction of about 4%. If rain stops and the material is wet (purple), there is no change for Exp. 1 and just a small effect for Exp. 2 (+2% $NO_x$ reduction). Obviously the water molecules block the active adsorption sites on the surface and therefore the photocatalytic degradation of the nitrogen oxides is almost completely suppressed. How strong the influence of the surface wetness is, is clearly shown in the last period of each experiment. Even if the light is turned off, there is just a very small change in the $NO_x$ values (±1%), demonstrating the importance of this parameter for the application of such photocatalytic material. After each experiment the aqueous extract of the plate was analysed by ion chromatography. As adsorbed products nitrite ($NO_2^-$) 19±4% and nitrate ($NO_3^-$) 81±4% were observed. The high nitrogen yield of about 100% confirms the absence of any significant other nitrogen containing product.

### Conclusion and Outlook

The first results using the developed ROR show the applicability of this new reactor to investigate photocatalysis of nitrogen oxides on a photocatalytic active concrete. By using the rain bars it is also possible to simulate rain and it could clearly be shown, that the wetness of the surface has a strong influence on the photocatalytic activity of the material. Based on these first results, it is planned to use the special ROR to perform experiments with different volatile organic compounds and to investigate a possible formation of low volatile photocatalytic reaction products on the surface of the material.