



A Life+ Demonstration Programme

## Demonstration of Photocatalytic Remediation Processes on Air Quality PhotoPaq

### **Life + PHOTOPAQ**

### **DELIVRABLE VI**

### **Field Campaign Strategy**

### **Action P3**

The general objective of the field campaigns included in the PhotoPAQ project is to assess on the field the effects of the photocatalytic materials on the air quality of the area where applied. This objective implies to set up a strategy which would allow us to obtain measurable effects which can then be extrapolated at larger scale.

The basic principle of the field campaigns as already defined in the proposal is to compare under very similar environments the effect of active surfaces with that of “normal” surfaces. Furthermore, for demonstration reasons the project is focused on two apparently opposite strategic objectives: on one side it is recommended to install the field sites in a very common environment (e.g. normal street, parking lot, tunnels...etc); on the other side it is mandatory to gather precisely measurable information on the pollutant losses and transformations on active surfaces in order to transfer it to the modellers. Based on the results from the laboratory tests, the literature and the request of the modelling activities, the role of the P3 action is to reconcile these aims.

## General strategy

Two possible strategies were possible and have been extensively discussed among the partners:

- 1 - Carrying out measurements before and after application of the material and from the difference in air quality obtained discuss the efficiency of the material by comparison. This approach which has already been chosen in other studies (Guerrini et al., 2012) has the advantage to be applicable for both indoor and outdoor sites. In addition, it is readily understandable by non-scientists and hence easily transferable to decision-makers.

On the other hand, considering the extremely high variability of the concentration of atmospheric pollutants and/or meteorological conditions, it would require to conduct measurements during very long periods to gather statistically meaningful information. This could be done when a limited set of instruments is deployed and when these instruments are designed for being operated in harsh environments without servicing or special attention. In the case of the PhotoPAQ project, the aim is a comprehensive qualification of the effects of active materials. This implies the deployment of a very large set of scientific instrumentation among which some instruments are of very high technology and require constant care. Furthermore, the application of “active” materials is generally carried out during larger renewal operations which often imply traffic modification or which can affect user’s habit. This may certainly affect local pollutants emission and the effect observed (positive or negative) could not be always related to the physico-chemical behaviour of the active surfaces.

- 2 - The second approach discussed was the deployment of two identical sets of scientific instruments in two measurement stations: one supposed to be under influence of air which has been in contact with the active surfaces, the other under influence of “normal” air, with air masses for both sites being similar to allow the comparison. This approach dedicates a significant role to air dynamics modelling to interpret the data and make the choice of a field site exhibiting a topography which can be modelled, rather critical.

The general strategy which has been adopted is clearly derived from the second approach (two sites). In addition to what was forecasted it has been decided to carry out some pre-campaigns before application where a limited set of instruments was deployed to keep the possibility of a before/after analysis and to better characterize the sites before the full campaigns. Furthermore, during the full campaign in the Brussels tunnel an “on/off” approach was followed with modulation of the installed UV lighting, to discriminate further between “active” and “non-active” periods of the applied photocatalytic materials (see further on).

## Definition of field sites

The definition of field sites is certainly one of the more critical actions of the “Strategic activities” of the PhotoPAQ consortium. Indeed, apart from the opportunities brought (or not) by the existence of civil engineering projects involving large scale application of the photocatalytic material, specific constraints have to be taken into account.

The two main constraints are that:

- the site should provide the maximum measurable effect of the applied material
- the aerology of the site should be implementable into dynamic models (see above).

To meet these requirements, it is necessary to work in an environment which exhibits high surface to volume ratio and which is strongly influenced by human activities in general and by traffic in particular. For comparison purpose, the geometry of the field site with and without active coating must be very similar.

Ideally, in order to have a measurable effect it is necessary to choose an environment in which streets

- exhibit a high building height to width street ratio
- are long enough
- allow high traffic load
- are not exposed to "open" urban structures (like parks, large crossroads, lakes etc...)

## Tunnel campaign strategy

### **General**

The first field site which has been chosen is an urban tunnel travelling underground below Brussels city centre: the Leopold II tunnel.

The Leopold II tunnel is a bi-directional tunnel located in the Brussels city centre along the Basilica – Midi axis, within a densely built urban environment (Figure 1).



**Figure 1: Leopold II tunnel pathway – In yellow the segment chosen as field site.**

The geometry of the overall tunnel is highly complex as it is about 2.3 km long and consists of two segments separated by a wall, with varying cross sectional areas along each direction.

The above described criteria have been applied to the tunnel to identify a suitable section.

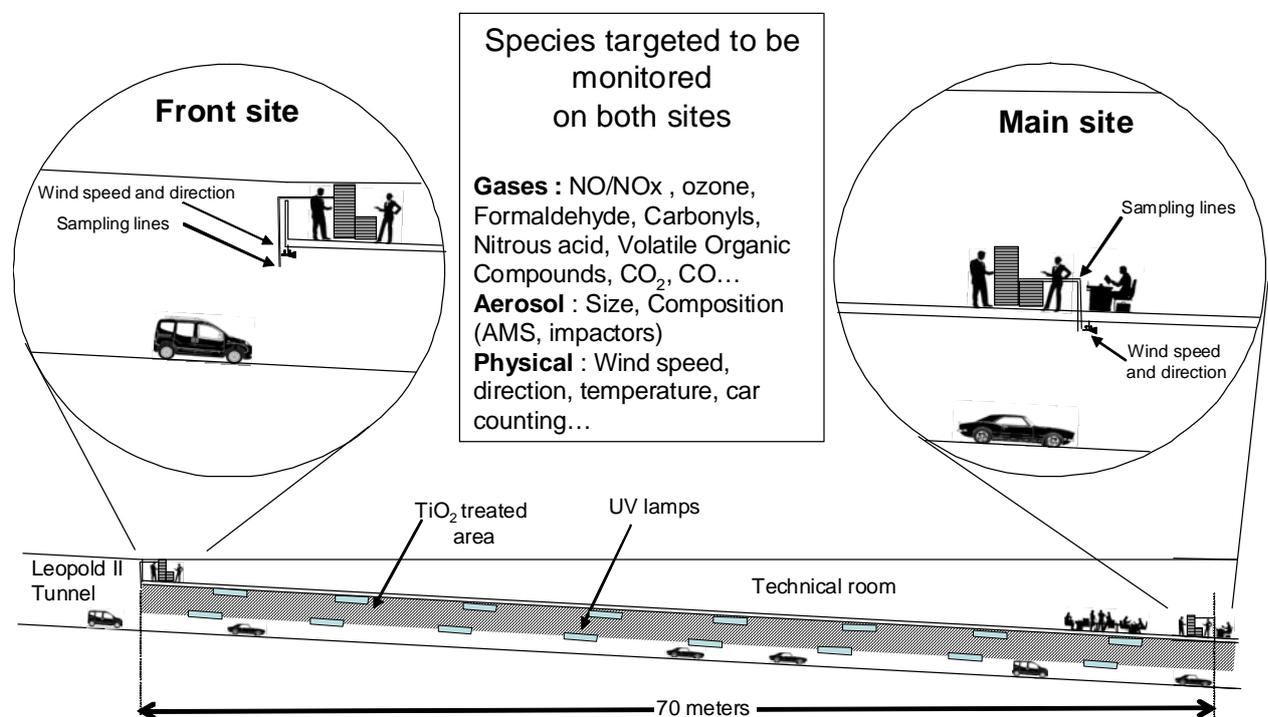
The tunnel is subject to a heavy traffic with a flow regularly reaching several thousands of vehicles per hour allowing us to have a sufficient level of pollutants. In spite of the complexity of the tunnel geometry, it was possible to identify a section of a length of 110 meters exhibiting a regular cross-section which enables a precise modelling of the air

flow. It should be noted that as both segments are separated by a wall, each one can be considered as a one-directional tunnel.

A large technical room has also been identified above the targeted section and holes in the ceiling of the tunnel have been used to allow the deployment of sampling lines and cables for the measurements.

To apply our strategy, two heavily instrumented monitoring stations have been set up (see figure 2). The first one – from now referred to as the front site – is the first to be encountered by an air mass when the flow of cars induces sufficient air movements. The measurements here are not considered to be affected by photocatalytic material effects in most of the time. The second one – referred to as the main site – is generally fed with air which has been in contact with photocatalytic materials.

Eventually, for some technical reasons (see I2 action report) only a section of 70 meters was covered with the photoactive coating.



**Figure 2: Schematic of the monitoring station built in the Leopold II tunnel for the first Brussels campaign (September 2011) – the airflow is following in most of the cases the car flow (i.e. here from the left to the right).**

## ***Compounds/Parameters to be monitored***

### **Gas phase measurements**

A series of gas phase measurement techniques have been targeted to be deployed on both sites (see figure 2). They include:

- NO/NO<sub>x</sub>: Nitrogen oxides are key species for air quality. They play a significant role in the oxidizing capacity of the atmosphere as propagating species for the photocatalytic cycles which lead to the accumulation of ozone (Finlayson-Pitts and Pitts, 2000). In addition, NO<sub>2</sub> is a regulated species for which target levels have been decided by the EU (European Parliament and the Council or the European Union, 2008). Furthermore, experimental evidences from P1 and P2 actions within PhotoPAQ have shown that nitrogen oxides are highly sensitive to

oxidation induced by photo-reactive materials. It is certainly among the most critical species to follow for the assessment in the field of the air cleaning efficiency of Photocatalytic surfaces.

- Formaldehyde: Formaldehyde is a toxic species also involved in photo-oxidation cycles for the transformation of air pollutants as initiating species. Experimental evidences from P1 and P2 actions within PhotoPAQ have shown that HCHO is highly sensitive to oxidation induced by photo-reactive materials but can also be produced during the oxidation processes of Volatile Organic Carbons (VOCs). It was hence necessary to monitor it on the field.

- CO<sub>2</sub>: Carbon dioxide is certainly not affected by TiO<sub>2</sub> containing surface since CO<sub>2</sub> is a very stable gas. Nevertheless, its monitoring was mandatory as a tracer of vehicles emissions to be able to normalize the observations (see below) and to compare if emissions are similar at both monitoring sites.

- Nitrous acid: HONO is a very important initiator of photo-oxidation cycles of air pollutants. It is generally produced by heterogeneous reactions. P1 and P2 actions have shown a significant production of HONO by photo-catalytic surfaces when this latter is not alkaline. In spite of a well established alkaline nature of the applied material in the tunnel but considering that HONO formation could be one of the major drawbacks of the TiO<sub>2</sub> de-polluting techniques, it has been decided to carefully monitor it on both sites of the tunnel.

- Ozone: As its reaction with NO is very fast, O<sub>3</sub> is unlikely to be found in significant concentration in a NO rich environment such as a freeway tunnel. Nevertheless, considering its major importance for air quality and the fact that a previous study has shown its production on TiO<sub>2</sub> surfaces (Monge et al, 2010), it was decided to monitor it on both sites of the tunnel.

- Volatile organic compounds (VOCs): Volatile organic compounds are a class of species which are also critical for photo-oxidation cycles that lead to harmful air pollutants (ozone, aldehydes, peroxyacyl nitrates, particles). Some of them such as aromatic species are directly toxic. Furthermore, experimental evidences from P1 and P2 actions within PhotoPAQ have shown that some VOCs are sensitive to oxidation induced by photo-reactive materials.

This class of species covers both primary emitted species and secondary produced compounds. It consists of several thousands of species. It would be hence certainly an illusion to aim at monitoring all these species. It has thus been decided to cover a selection of light and heavier primary VOCs by deploying adequate techniques (GC-FID and GC-MS after sorbent cartridges sampling) and, on the other hand, for secondary (oxidized) species specific techniques were applied (HCHO monitor and DNPH-derivatization HPLC)

## **Aerosol phase measurements**

So far, neither lab nor field works have shown any effect of TiO<sub>2</sub> doped material on aerosol chemistry. Nevertheless, it has been hypothesized from the initial PhotoPAQ proposal that the early oxidation of organic matter or its capture by surface reactions could affect the aerosol formation or ageing. Hence, it has been decided to include some physical and chemical characterisations of the aerosol into our strategy. To do so, the deployment of high technology instruments such as aerosol mass spectrometers (AMS) giving access to both aerosol size distribution and quantity in the nanomode and to bulk chemical characterization has been opted in parallel with the use of up-to-date impactor techniques (Berner impactors). In addition, black carbon measurements were performed using a Multi-Angle Absorption Photometer (MAAP).

## **Physical parameter measurements**

It has been identified that air flow modelling is certainly a key point to interpret the data resulting from the Brussels tunnel campaign. In consequence, two wind speed /direction

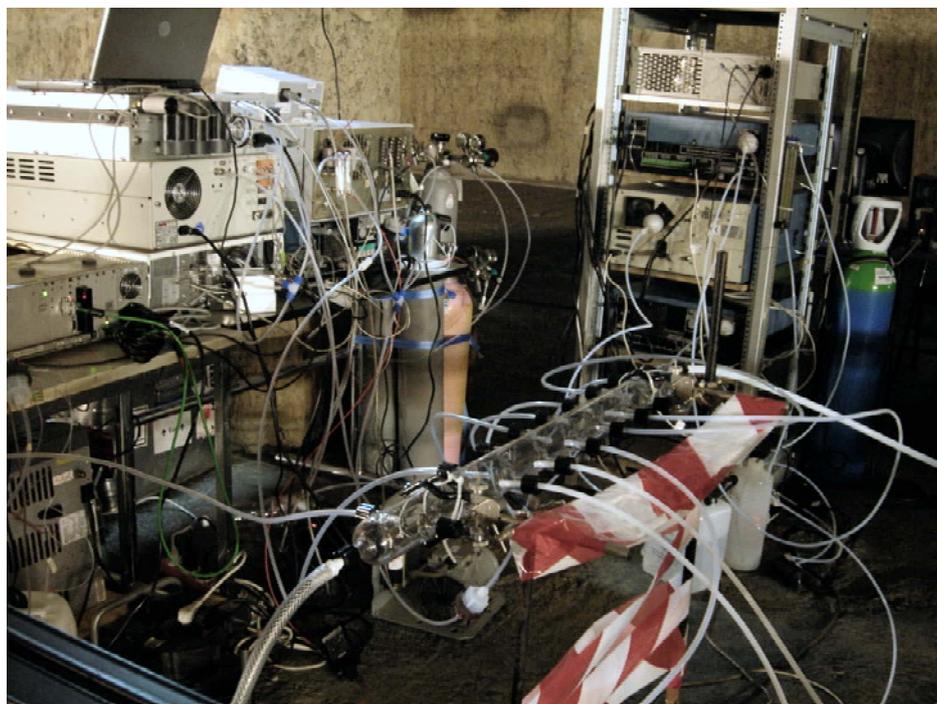
sensors were installed near the exits of the sampling line. These sensors were also equipped with temperature and relative humidity sensors.

It has also been considered that characterizing the light flux received by the treated surface was a priority. Spectroradiometric measurements were thus conducted to determine spectral irradiance as received by the walls/ceilings.

### ***Sampling strategy***

The general strategy for sampling was based upon three criteria: i) choosing appropriate sampling lines ii) ensuring the representativeness of the measurements iii) organizing the co-localisation of sampling.

In both sites, the sampling of gases was achieved through a unique ½” outer diameter pipe made of PTFE to insure chemical inertia. All the instruments were connected to a glass manifold with ¼” PTFE tubes. At one extremity the manifold was connected to the sampling line in the tunnel and, at the other end, it was connected to a pump in order to have a sufficient flow to minimize the residence time. Indeed, it has been identified that minimizing the residence time was necessary to limit the chemical evolution of the air mass sampled.



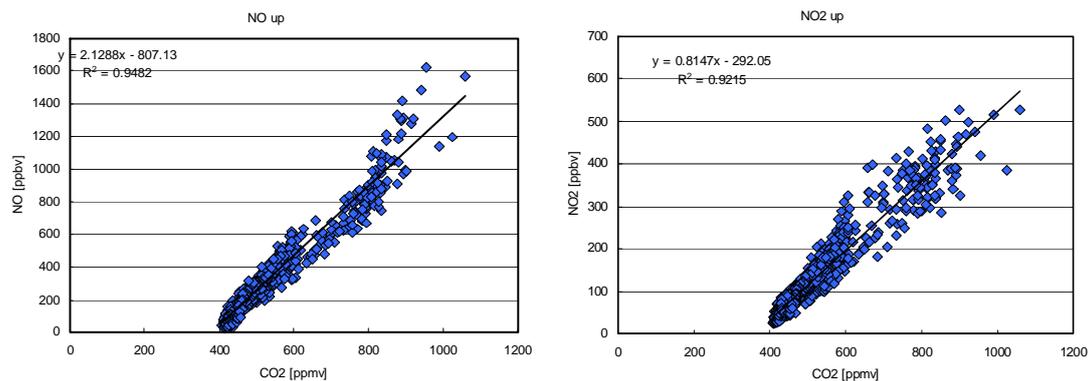
**Figure 3: View of the gas phase manifold at the main site**

This configuration allowed some flexibility, since instruments could be added anytime to the ports which are not used or these ports can be closed. At the other end, the sampling line from the inlet to the manifold was about 6 meters.

For aerosol sampling, PTFE was not permitted due to its electrostatic properties which lead to losses inside the tubing: here, a stainless steel ½” outer diameter pipe was installed. The large diameter was also chosen to minimize losses.

## Data analysis strategy

As already mentioned above, the basic strategy for the data analysis, is to compare front station with main station measurements. Nevertheless, this approach can not be carried out directly as it is not possible to consider that emissions are negligible between both sampling sites. To apply this approach, it is hence necessary to standardize the data using CO<sub>2</sub> as a tracer for emission. Indeed, so far no abatement has ever been noticed for CO<sub>2</sub> over photocatalytic materials while it is quite well known that the emission indices (EI) by vehicles for CO<sub>2</sub> can be considered in the range of 3150 g/kg of burnt fuel and being approximately independent on type of fuel. This hypothesis was somewhat validated by the results of the pre-campaign carried out in the Brussels tunnel. As an example, the linear regressions presented in figure 4 support these assumptions.



**Figure 4 : NO<sub>x</sub> (NO and NO<sub>2</sub>) as a function of CO<sub>2</sub> as measured (partners BUW and BRRC) during the pre-campaign held in the Leopold II tunnel in June 2011.**

In consequence, for a given pollutant X, the X/CO<sub>2</sub> ratio can be used to calculate emission indices. Our strategy is based on the hypothesis that this ratio will change between front site and main site if photocatalytic degradation (or production) of X is occurring significantly between both sampling stations. This approach will then be applied to all the compounds monitored at both sites in order to track any change in the slope of these plots.

Besides this approach which constitutes our main strategy, a secondary data analysis methodology has been identified. For some specific measurements which would not be available in both sites, it has been decided to install the related instrument on the main site. A *light on/light off* methodology has then been defined. Indeed, photocatalytic effects of the studied material involve activation by UV light. It is hence assumed that a comparison of X/CO<sub>2</sub> ratios during light and dark periods should allow identifying additional effects of the application of a TiO<sub>2</sub> containing coating.

## Outdoor campaigns strategy

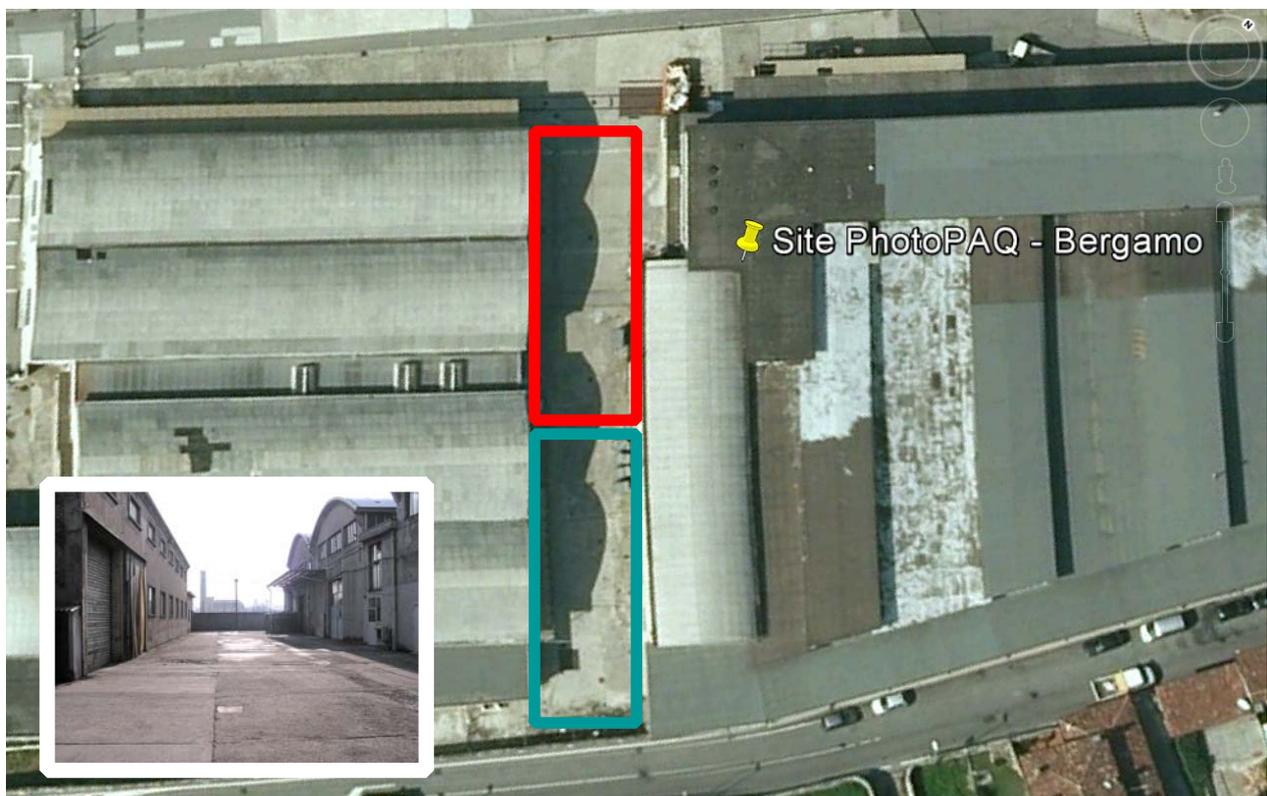
### General

The choice of the outdoor field campaign site has been the subject of many investigations and discussions. With the help of satellite imaging, the information available from the civil engineering companies in charge of the related urbanisms projects and information available to the consortium, many potential sites have been carefully studied. Eventually, a field site in southern Europe (Bergamo, Italy) was chosen. Here a dual field site with high surface-to-

volume ratio will be constructed (based on the existing industrial facility) and equipped in an urban area.

About the open field site campaign, while it has been forecasted to conduct measurements in both the northern and the southern Europe, this strategy does not seem to bring additional demonstrating clues anymore. Indeed, from the P1 and P2 actions the effect of sunlight has been very well characterised and two outdoor field campaigns would not bring additional evidence or parameterization. On the contrary, it seems now obvious that finding an adequate site with suitable surface-to-volume ratio and accounting for micro-aerology is really one of the key points of the demonstrating process. In consequence, based on the P3 action works, the consortium has decided to focus the PhotoPAQ field campaign on investigating this latter category of parameters.

The field site chosen in Bergamo (Italy) is a former industrial area. In this site, a street canyon will be simulated in a factory yard. This yard is ca. 60 meters long by 10 meters wide and is surrounded with 10 meter height walls (see figure 5)



**Figure 5: View of the Bergamo site. The insert shows the backyard before any construction and application. The rectangles show the proposed “active” (i.e. covered) and “non active” areas.**

The experience acquired during the tunnel campaign preparation and analysis has shown that the work on the field strategy is clearly deeply linked with the field actions. Indeed, adjustment of the field strategy has to be carried out until the very last days before the campaign to take advantages from local opportunities. Considering that the agenda for field actions has been extended, an extension of the P3 action until May 2013 is required. *The strategy described below is hence subject to possible addendum which can be submitted at a latter stage of the project.*

### ***Compounds/parameters to be monitored***

The criteria which have been cited for the species targeted for the Brussels tunnel campaign remain totally valid for this campaign. In consequence, the list of compounds and parameters remain practically unchanged.

Only the average levels of concentration are expected to be significantly smaller. To evaluate this, three years of measurement from ARPA Lombardia (the organisation in charge of the air quality monitoring) taken via Garibaldi, Bergamo (1.6 km away from the field site) have been analysed. Furthermore, a special care will be taken to measure solar irradiance at surfaces as the change in solar flux induced by the change of the zenith angle along the day or by the weather will have to be taken into account during data analysis.

### ***Demonstration strategy***

In this case, the demonstration strategy relies on the building of two identical areas on the field site delimited by walls. One will receive the application of the photocatalytic coating while the other not. Two similar measurement stations will be installed in both sub-yards and parallel measurements will be carried out. The demonstration of the efficiency of the photocatalytic air cleaning will be performed by comparison of both sets of measurements.

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