

Impact of Photocatalytic Paint on NO₂ Levels in a Heavily Polluted Area in Metro Manila



A study carried out at Guadalupe MRT station along EDSA during 2009.

The purpose of this preliminary report is to, in a summarized way, describe the results of a measurement campaign to study the impact on NO₂ pollution levels from photocatalytic paint applied on the walls at the MRT station. I.e., would photocatalytic paint be a way to reduce the negative health effects of high level NO₂ exposures caused by traffic and other pollution sources?

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PRELIMINARY version

0 Summary

NO_x is a generic term for mono-nitrogen oxides (NO and NO₂). These oxides are produced during combustion; especially combustion at high temperatures like in a vehicle engine. NO_x reacts with volatile organic compounds in the presence of heat and sunlight to form ozone. NO_x also reacts with other compounds to form nitric acid vapor and related particles.

Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases such as emphysema and bronchitis, and it may also aggravate existing heart disease. Low level NO₂ exposure may cause increased bronchial reactivity in some asthmatics, decreased lung function in patients with chronic obstructive pulmonary disease and increased risk of respiratory infections, especially in young children. Continued exposure to high NO₂ levels can contribute to the development of acute or chronic bronchitis. Long-term exposure to NO₂ at concentrations above 40 - 100 µg/m³ causes adverse health effects.

NO₂ (nitrogen dioxide) was measured at Guadalupe MRT station using “Passive Samplers” or “Diffusive Sampling Technique”. Guadalupe MRT station is located along EDSA with its heavy traffic with some days over 180,000 vehicles. The design of the MRT station and the surroundings allow for representative location of monitoring locations.

There were 19 monitoring locations divided into background locations (non-photocatalytic painted areas for reference purposes), curb side locations (close to the pollution source), upper level locations (better ventilation than on the street level), and one indoor location (office). 13 of the outdoor locations were painted with photocatalytic paint and 5 were painted with non- photocatalytic paint. The locations demonstrate a varying degree of confinement, exposure to prevailing winds, and sunlight. Almost all locations were chosen to reflect the air that people breathe; either as pedestrians, commuters, or working in the area.

Traffic is estimated to contribute to around 80% of the NO_x emissions in Metro Manila. Meteorological conditions play a large role in the actual pollution concentrations at street level. In order to keep both factors under control the number of vehicles and meteorological parameters were measured. The traffic, i.e. the emissions of NO₂, was relatively stable during the whole trial.

The measured levels of NO₂ were very high. The Philippine Air Quality Guideline for NO₂ for 24-hour means is 150 µg/m³ while the European Union Guideline for NO₂ annual means is 40 µg/m³. The Philippine Guideline was exceeded during a large part of the time while the European Guidelines was exceeded during the whole period.

The preliminary results indicate a significant difference in reduced pollution levels both between areas painted with photocatalytic paint and ordinary paint on the one hand, and how the areas are facing west/windward and east/leeward on the other hand.

The results show pollution reduction effects between 23% compared to the background on west/windward walls down to low measurable reduction effects for east/leeward walls.

Upcoming local scale dispersion modelling will be used to further determine the reasons for the differences.

1 Health Aspects

NO_x is a generic term for mono-nitrogen oxides (NO and NO_2). These oxides are produced during combustion; especially combustion at high temperatures like in a vehicle engine.

NO_x reacts with ammonia, moisture, and other compounds to form nitric acid vapor and related particles. Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases such as emphysema, and bronchitis; and it may also aggravate existing heart disease.

NO_x reacts with volatile organic compounds in the presence of heat and sunlight to form ozone. Ozone can cause adverse effects such as damage to lung tissue and reduction in lung function mostly in susceptible populations (children, elderly, asthmatics). Ozone can be transported by wind currents and cause health impacts far from the original sources.

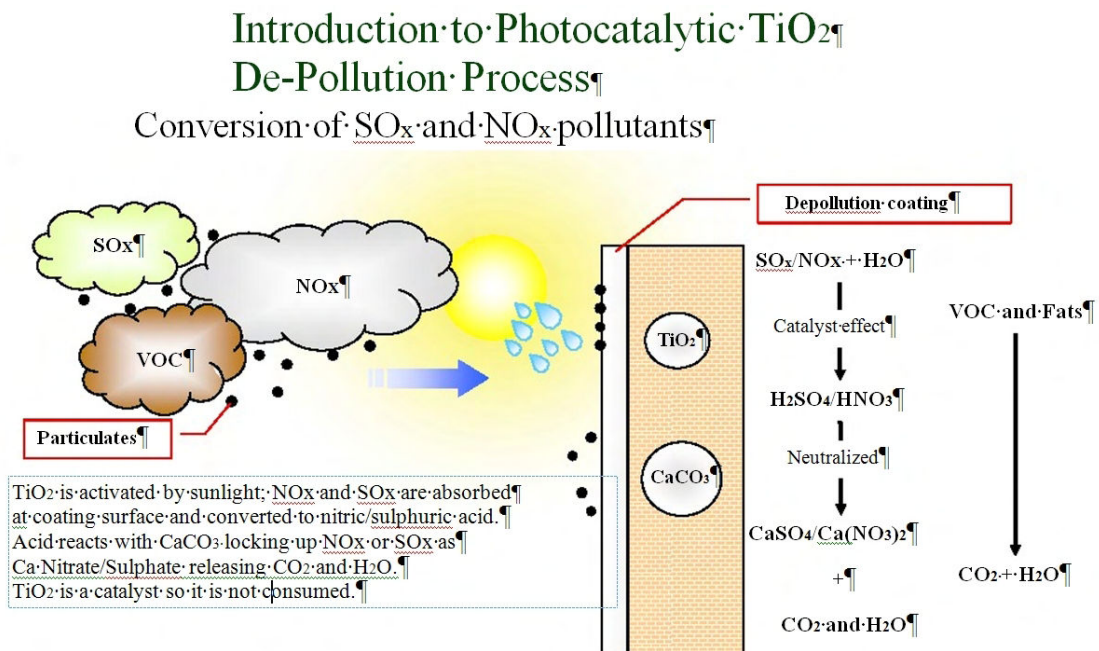
NO_x also readily reacts with common organic chemicals, and even ozone, to form a wide variety of toxic products: nitroarenes, nitrosamines and also the nitrate radical some of which may cause biological mutations.

NO_2 (nitrogen dioxide) acts mainly as an irritant affecting the mucosa of the eyes, nose, throat, and respiratory tract. Extremely high-dose exposure (as in a building fire) to NO_2 may result in pulmonary edema and diffuse lung injury. Continued exposure to high NO_2 levels can contribute to the development of acute or chronic bronchitis. Low level NO_2 exposure may cause increased bronchial reactivity in some asthmatics, decreased lung function in patients with chronic obstructive pulmonary disease and increased risk of respiratory infections, especially in young children.

Long-term exposure to NO_2 at concentrations above 40 - 100 $\mu\text{g}/\text{m}^3$ causes adverse health effects¹.

2 Principles for photocatalytic paint

How photocatalytic paint works in the de-pollution process is briefly described in the picture below.



The reaction is instantaneous.

¹ US EPA

3 Monitoring

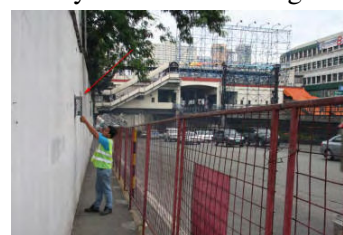
3.1 Choice of location

To ensure that the monitoring in the project really measured the differences over time in areas painted with photocatalytic paint compared to the ones painted with ordinary paint, a comprehensive monitoring program was accomplished. The Swedish consultancy company Conexor AB², specializing in ambient air quality projects, designed and followed up the monitoring and the results.

There was a need to optimize several, partly conflicting, issues like representativity (painted vs non-painted areas), control of emissions (the source of the pollution), and practical questions like accessibility and security.



Guadalupe MRT station along EDSA was chosen for the trial. Guadalupe MRT station is located along EDSA with its heavy traffic. The design of the MRT station and the surroundings allow for representative locations of monitoring sites.



There were 19 monitoring sites divided into:

- Background sites (ordinary or not painted locations for reference purposes), five locations;
- Curb side sites (close to the pollution source), nine locations ;
- Upper level sites (better ventilation than on the street level), four locations; and
- Indoor site (office), one location.

13 of the outdoor locations were painted with photocatalytic paint and 5 (background locations and the indoor office location) were painted with non-photocatalytic (ordinary) paint or not painted at all. The locations have a varying degree of confinement, exposure to prevailing winds, and sunlight.



The numbers and colors indicate the various locations and “lines” along which the monitoring was accomplished. The yellow line is the “background” area (#16, #17, and #18) around 250 meters south of the MRT station and the photocatalytic painted areas. Also #01 and #10 are background locations painted with ordinary paint.

² www.conexor.com

3.2 Meteorology

Meteorological factors play a very important role in how the emissions from traffic (and other sources) are dispersed and distributed. Hence, a meteorological mast was placed on the roof of Guadalupe MRT station. The mast measured all parameters of importance to allow for later determination of the impact of the local meteorological conditions on the monitored NO₂ values.

The data will be used for the upcoming local scale dispersion modeling.

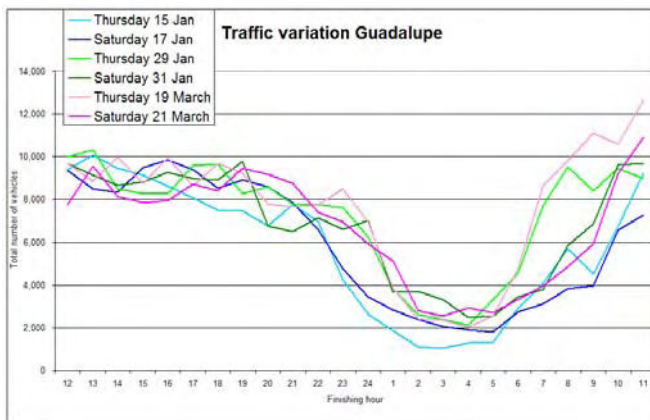
3.3 Traffic

Traffic is estimated to account for around 80% of the NO_x emissions in Metro Manila³. The traffic counting was divided into six 24-hour batches (11 am – 11 am) and 20 different vehicle categories like Passenger Cars, Owner Type Jeeps, Large Buses (City/Provincial), and Rigid Trucks (2-axle). The counting was carried out manually with staff from the National Center for Transportation Studies in University of the Philippines Diliman.



The six 24-hours batches with hourly counting of all the 20 different vehicle categories were

- 15 (Thursday) -- 16 (Friday) January and 17 (Saturday) -- 18 (Sunday) January, 2009;
- 29 (Thursday) -- 30 (Friday) January and 31 (Saturday) January -- 01 (Sunday) February, 2009; and
- 19 (Thursday) -- 20 (Friday) March and 21 (Saturday) -- 22 (Sunday) March, 2009.



The maximum number of vehicles, over 184,000, was measured on Thursday 19 March, 2009 and the least number of vehicles was on Thursday 15 January 2009 with just below 138,000. The overall traffic variation was relatively consistent for all six batches. There was a clear daily pattern and the volume of traffic was not varying much between the periods.

Hence, the emissions of NO₂ were relatively stable during the trial.

3.4 NO₂

NO₂ (nitrogen dioxide) was measured using “passive samplers” or “diffusive sampling technique”.

The diffusive sampling technique is a useful tool for the determination of e.g. geographical distributions of air pollutants and their variations over time.

The samplers give an average pollution level for the monitoring period. Hence, if the measurements are carried out between from 11 am one day to 11 am the following day, it is easy to compare the results with e.g. 24-hour ambient air guidelines.

³ World Bank Report: Urban air quality management strategy in Asia : Metro Manila report. Shah, Jitendra J. and Nagpal, Tanvi [editors]. Report Number: WTP380



The technique is based on the concept of diffusion. In diffusive sampling the gas is transported by turbulent diffusion through the open end into the absorbent where the gas is absorbed by the sampling medium through molecular diffusion.

This is a net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion. The result of diffusion is a gradual mixing of material. In a phase with uniform temperature (and no external net forces acting on the particles) the diffusion process will eventually result in complete mixing or a state of equilibrium.

From Fick's law⁴ it can be calculated that the trapped amount is directly proportional to the ambient pollutant concentration, the exposure time, the diffusion coefficient in air for the pollutant in question, and the cross-sectional area of the tube. The collected amount is further inversely proportional to the distance that the gas has to pass by molecular diffusion. The average sampling rate (absorbed amount per unit time divided by the ambient concentration e.g. ml/min) is a temperature-dependent constant for a given pollutant and sampler.

The samplers are provided in different models depending on the manufacturer. Generally they consist of a tube which has a cap on one end containing a filter which is impregnated with a solution specific to absorb the pollutant to be measured. The gas is transported into the tube through the open end by molecular diffusion (as described above.)

The samplers are protected from the impact of weather (strong wind, precipitation, sun shine, etc) by a shelter. The samplers are easy to handle, small, light, soundless, and do not require electricity or calibration in the field. Each sampler gives average air concentration with continuous time coverage up to a month. In this project the monitoring periods were 24 hours (11 am -- 11 am the following day).

The diffusive sampler can be used for measurements of a variety of air pollutants. In this project only NO₂ was measured.

The samplers were collected at the site, thoroughly marked and sealed at the monitoring site, and then brought to the laboratory for analyzes.

In this project, diffusive samplers from Ogawa & Co., USA, Inc.⁵ were used.



4 Analyses

The Philippine Institute of Pure and Applied Chemistry (PIPAC) has carried out the analyses. PIPAC is accredited under ISO/Guide 25, which attests to the high standard of competence in the analytical laboratory maintained by PIPAC.

The samplers were collected at the site and thoroughly marked. The samples filters were thoroughly sealed and marked at the monitoring site, and then brought to PIPAC. Since the amount of samples was very high, the logistics became a crucial issue. The analyses protocol from Ogawa was followed in detail. At least three blanks for each batch were analyzed.



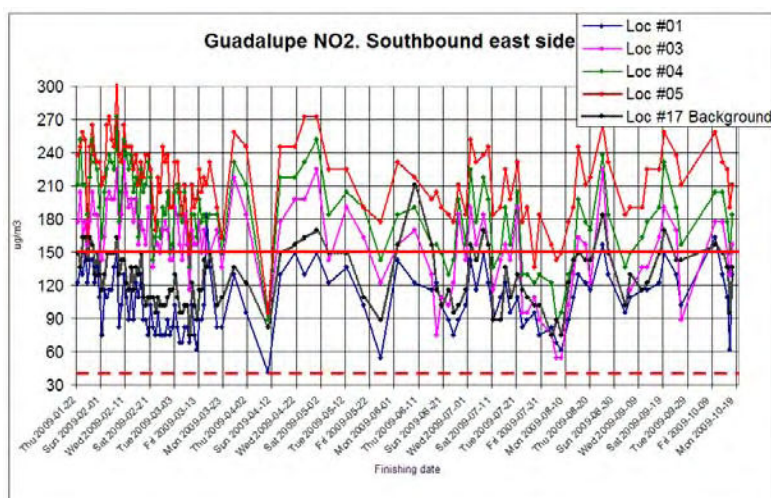
⁴ Fick's first law relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient

⁵ www.ogawausa.com/passive.html

5 Monitoring results

The monitoring of NO₂ was carried out during January -- October 2009 as 24-hour averages. 2,307 samples were analyzed which probably makes this trial the most comprehensive ever of its kind. The measured levels of NO₂ were very high. The variation over time was also very high: Average value = 126; Standard deviation = 51; Maximum value = 306; Minimum value: 27.

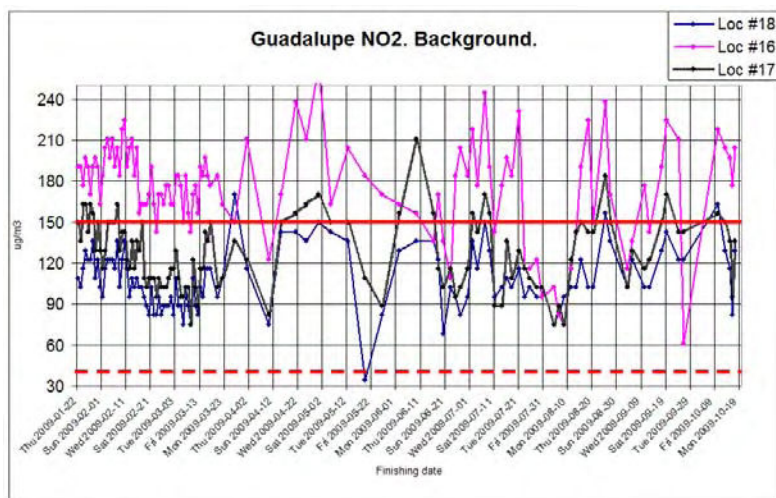
The Philippine Air Quality Guideline⁶ for NO₂ for 24-hour means is 150 µg/m³. This level is indicated by the red line in the graphs below. The European Union Guideline for NO₂ annual means is 40 µg/m³ and is indicated by the dashed red line.



The graph shows the monitoring results for some of the locations.

As can be seen the Philippine Guidelines are exceeded during a large part of the time, while the European Guidelines (albeit an annual mean) were exceeded during the whole period.'

The dips can mostly be explained by either very low emissions (limited traffic) like April 10, 2009 (Good Friday) or very windy/rainy conditions (end of July 2009).



(The data is presented as "raw" data, which means that some "outliers" that might be incorrect data are not excluded.)

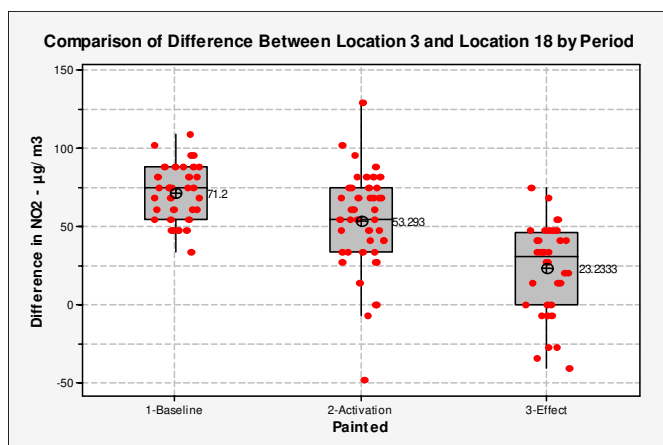
The dates are given in yyyy-mm-dd format.

The photocatalytic paint has an activation period of a few months under outdoor conditions in Metro Manila before it reaches the effect time. Since the variation between the different sites and also within data from the same site was very high, the "Boxplot" type of analyzes and presentations has been chosen.

In descriptive statistics, a boxplot is a convenient way of graphically depicting groups of numerical data through their five-number summaries: the smallest observation (sample minimum), lower quartile (Q1), median (Q2), upper quartile (Q3), and largest observation (sample maximum). A boxplot may also indicate which observations, if any, might be considered outliers.

Boxplots display differences between populations without making any assumptions of the underlying statistical distribution; hence, they are non-parametric. The spacings between the different parts of the box help indicate the degree of dispersion (spread) and skewness in the data, and identify outliers.

⁶ According to the Clean Air Act (Republic Act 8749)



Location	% Reduction				Ave
	Loc 1	Loc 10	Loc 17	Loc 18	
3	23.3	22.0	21.1	26.7	23.3
4	20.4	19.7	18.9	23.6	20.6
5	10.8	9.8	9.1	13.4	10.7
8	9.8	7.7	6.2	15.2	9.7
8(Act)	21.7	17.4	17.5	19.5	19.0
9	1.7	-0.1	-1.0	4.8	1.4
9(Act)	4.3	1.0	1.1	2.4	2.2
12	2.9	-0.5	-3.0	11.5	2.7
12(Act)	18.6	11.7	11.9	15.1	14.3
14	11.3	9.7	8.5	15.4	11.2
15	3.3	1.1	-0.6	8.9	3.2

Note Locations with (Act) are difference against the Activation period due to anomalies in the baseline period.

The table – as a box plot for the three periods (baseline, activation, effect) – indicates the reductions in NO₂ concentrations levels between location #03 (entrance of tunnel; indicated by red arrow on the front page) and the background location #18.

An average reduction of 23% was noted.

The table indicates the reductions (%) in NO₂ concentration levels between some locations and background locations.

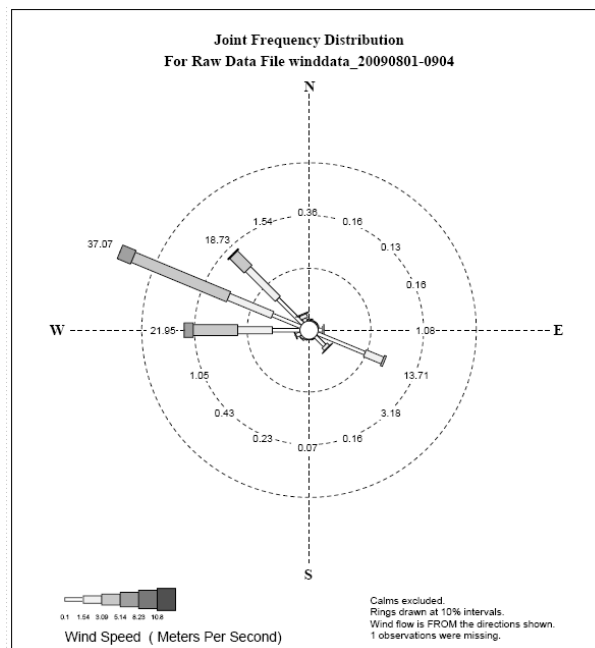
Locations #01, #10, #16, #17, and #18 are background locations.

The results for most of the other locations compared to background locations are listed in the table above. The reasons for the variation in reduction of pollution concentrations between the different locations are currently being evaluated and explained with, among other methods, the help of local scale dispersion modelling.

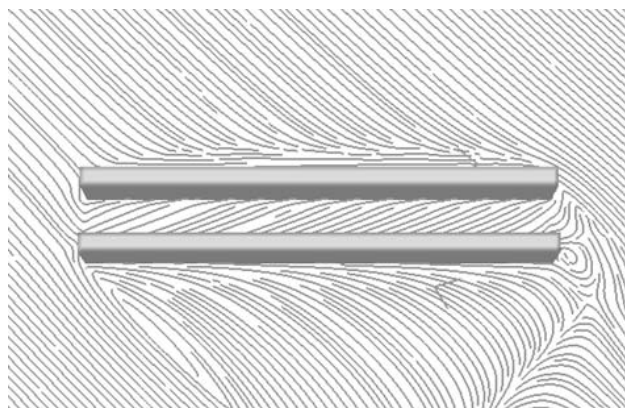
However, preliminary evaluations suggest that the direct exposure to influx of pollution, i.e. whether the wall faces windward or leeward plays an important role when it comes to monitored pollution reduction levels. The wind pattern during the effect period is relatively stable (see figure to the right showing the wind rose for August 2009). Most of the effect time, the wind blows from the north-western sector with zero to low (less than 3 m/s) wind speeds. This means that there is a channelling effect along the river and the different walls, which mainly run north-south, will – principally – be facing either windward or leeward.

The monitoring results in the table above indicate that the locations along the walls facing west, i.e. windward (#03, #04 (indicated by the red arrow inside the tunnel on the first picture on page 4), #05, and #08) show significantly higher reductions in pollution levels than the “corresponding” locations on the walls facing east, i.e. leeward.

The most striking example is differences between location #09 (facing east/leeward) with low measured reduction effect and location #08 (facing west/windward and also partly confined) showing a high level of pollution reduction. Both locations were painted with photocatalytic paint.



However, it is most important to point out that the pollution reduction effects on the leeward walls might very well be just as effective as those on the windward walls.



The local dispersion conditions along windward walls are different compared to the conditions along leeward walls. Hence, since the trial measured the ambient air quality as a time average, the local dispersion might create variations in the monitored values although the instantaneous pollution reduction effect might be the same.

The picture displays an example of local dispersion conditions along walls. The wind is blowing from northwest (i.e. from the upper left).

The upcoming local scale dispersion modelling will be able to determine the detailed conditions at Guadalupe MRT station and the variations in detected pollution reductions might be possible to explain from that.

6 Conclusions

The trial has demonstrated that photocatalytic paint has a reducing impact on the pollution levels of NO₂.

The preliminary results indicate a significant difference in reduced pollution levels both between areas painted with photocatalytic paint and ordinary paint on the one hand, and how the areas are facing west/windward and east/leeward on the other hand.

The results show pollution reduction effects between 23% compared to the background on west/windward walls down to low measurable reduction effects for east/leeward walls.

Upcoming local scale dispersion modelling will be used to further determine the reasons for the differences.

In order to further test the pollution reduction impact of photocatalytic paint under various conditions it is recommended to carry out a trial along the basic principles that have been used in the Guadalupe trial – but in an environment with a more “mixed air” and no direct exposure to winds causing windward/leeward conditions. A parking garage would provide a confined volume where the emissions could be controlled by the number of vehicles entering.