Environ Monit Assess (2008) 136:35–44
DOI 10.1007/s10661-007-9722-2

Photocatalytic degradation of NOx in a pilot street canyon configuration using TiO_2-mortar panels

Th. Maggos · A. Plassais · J. G. Bartzis · Ch. Vasilakos · N. Moussiopoulos · L. Bonafous

Received: 27 July 2006 / Accepted: 18 December 2006 / Published online: 12 June 2007

Abstract Titanium dioxide is the most important photocatalysts used for purifying applications. If a TiO_2- containing material is left outdoors as a form of flat panels, it is activated by sunlight to remove harmful NOx gases during the day. The photocatalytic efficiency of a TiO_2-treated mortar for removal of NOx was investigated in the frame of this work. For this purpose a fully equipped monitoring system was designed at a pilot site. This system allows the in situ evaluation of the de-polluting properties of a photocatalytic material by taking into account the climatologic phenomena in street canyons, accurate measurements of pollution level and full registration of meteorological data The pilot site involved three artificial canyon streets, a pollution source, continuous NOx measurements inside the canyons and the source as well as background and meteorological measurements. Significant differences on the NOx concentration level were observed between the TiO_2 treated and the reference canyon. NOx values in TiO_2 canyon were 36.7 to 82.0% lower than the ones observed in the reference one. Data arising from this study could be used to assess the impact of the photocatalytic material on the purification of the urban environment.

Keywords Photocatalysis · TiO_2 building materials · Pilot street canyon · NOx degradation · Meteorology

T. Maggos (✉) · C. Vasilakos
Environmental Research Laboratory, INT-RP,
NCSR "Demokritos",
153 10 Aghia Paraskevi,
Athens, Greece
e-mail: tmaggos@ipta.demokritos.gr

A. Plassais · L. Bonafous
CTG/Italcementi Group, Rue des Technodes,
78931 Guerville, France

J. G. Bartzis
Department of Energy Resources Engineering,
University of Western Macedonia,
51100 Kozani, Greece

N. Moussiopoulos
Laboratory of Heat Transfer and Environmental
Engineering, Aristotle University,
GR-54006 Thessaloniki, Greece

Introduction

Advanced oxidation technologies and more specifically heterogeneous photocatalysis represent emerging environmental control options for efficient removal of chemical pollutants. Among the various semiconductors TiO_2 in the form of anatase has attracted wide interest, due to its strong oxidizing power under U.V irradiation, its chemical stability and the absence of toxicity (Fujishima et al. 1999; Agrios and Pichat 2005; Lewandowski and Ollis 2004; Pichat 2003; Ibrahim and Lasa 2002; Zhang et al. 2001).

The development of innovative materials that can be easily applied on facades, with both de-soiling and de-polluting properties would be a significant step towards beautification of cities and improvements of air quality. The use of TiO_2 photocatalyst in combination with cementitius and other construction materials has shown a favorable effect in the removal of air pollutants (Fujishima et al. 1999). In recent years, a wide number of laboratory scale tests have been performed, under different experimental conditions, in order to evaluate the de-polluting properties of TiO_2 photocatalytic materials (Strini et al. 2005; Ao et al. 2003; Dalton et al. 2002; Blake 2001; Pichat et al. 2000). Accordingly, some local governments of cities that suffer from NOx pollution like Tokyo and Osaka have started evaluating the performance of photocatalytic air-purifying materials on larger scales. Field tests shows that building materials which can be used for applications such as in roadway structures or as outer materials on buildings could achieve passive air purification (Kaneko and Okura 2002). Regarding lab scale tests, experimental conditions are not representative of the environmental conditions, providing sometimes overestimate results on the photocatalytic properties of a material. On the other hand, during real life tests, a significant number of unknown parameters (i.e meteorological, human activities, air pollutants variety, street configuration etc) arise difficulties on the establishment of quality and assurance measuring procedures and results.

The purpose of this study is to measure the photocatalytic properties of a construction material

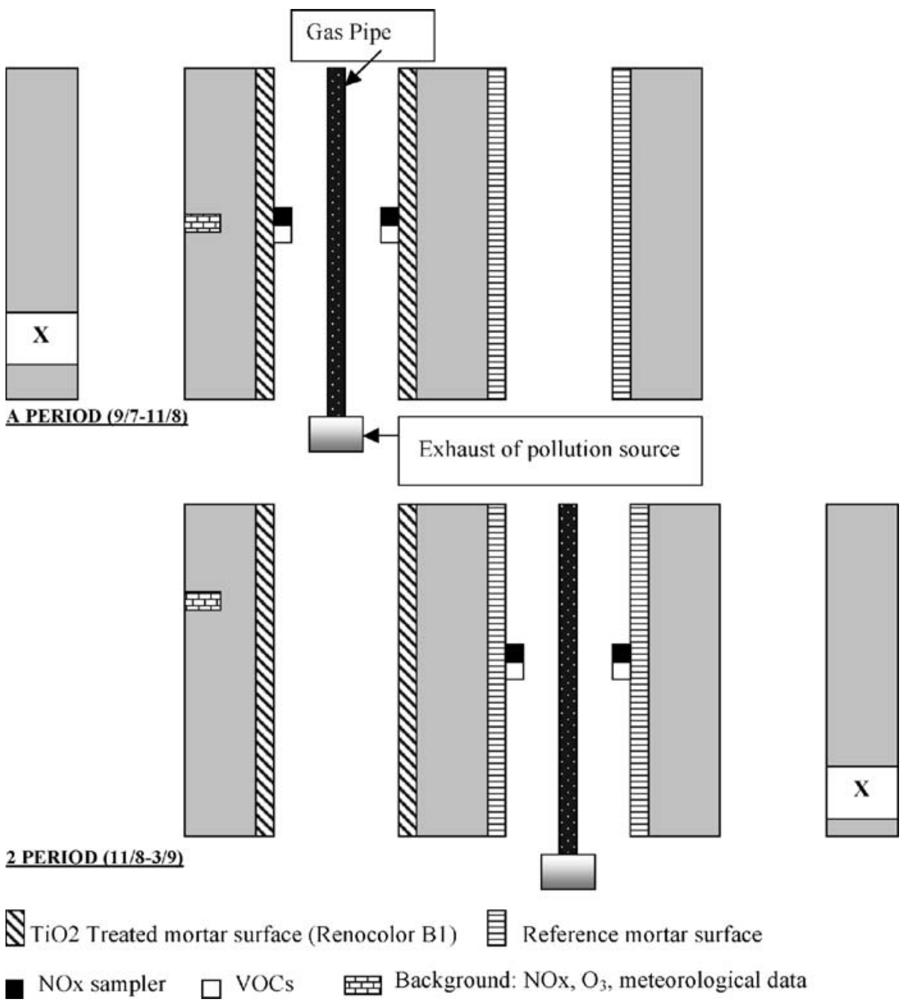


Fig. 1 Pilot site configuration

under real environmental conditions but controlled pollution and street geometry conditions. This experiment is an intermediary step between lab and real scale test in order to eliminate unreal and complicate conditions respectively.

For the purpose of the current experiment a TiO_2-containing mix mortar for external covering treated with was spread over the surface of panels. These panels were placed on the walls of an artificial 20 m canyon street, while panels with the same material but without (w/o) TiO_2 were placed on the walls of the other artificial street canyon (reference). A specially designed monitoring system was established on site. The efficiency of the material to remove NOx under natural conditions was evaluated from the difference of the pollution level in each canyon. The appropriate design of the experiment for pollutants and meteorological parameters monitoring was of great importance in order to obtain qualitative and representative results.

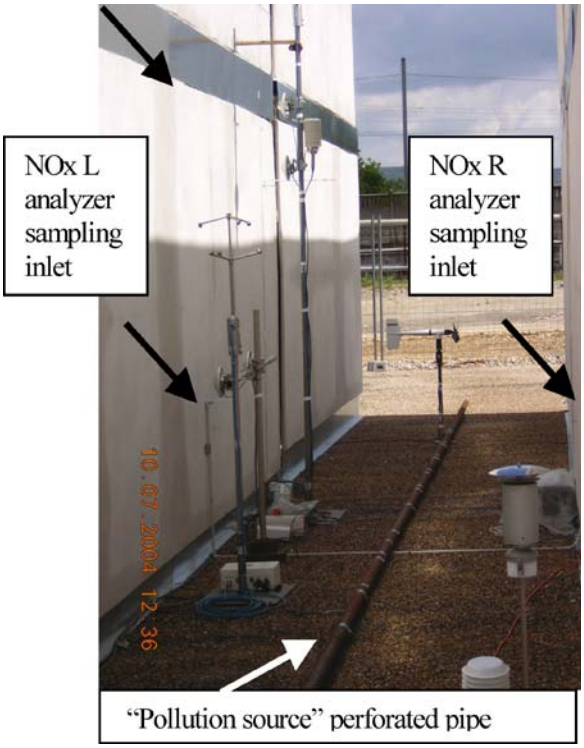


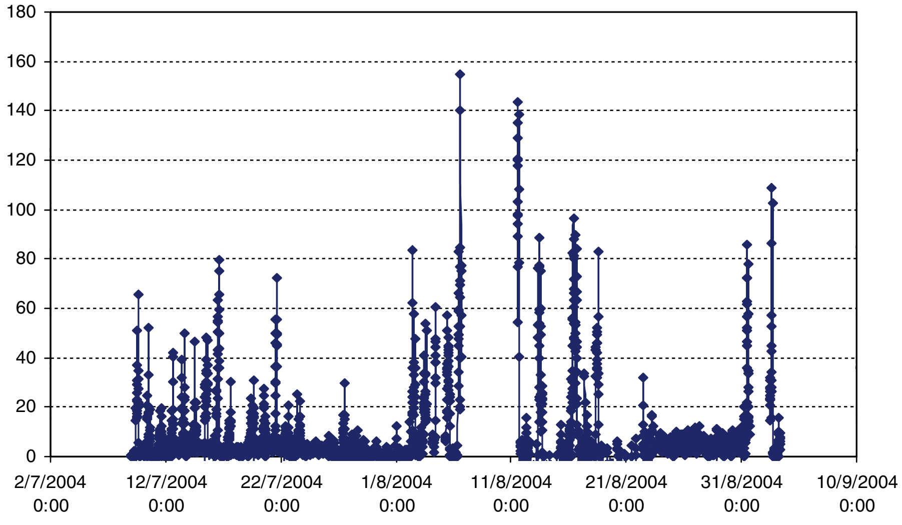
Fig. 2 Part of instrumentation in TiO_2 canyon

Methodology

Description of the pilot site configuration

A pilot site for testing the depollution efficiency of a TiO_2-containing cement material was established in CTG cement plant in Guerville, France. The site involves a series of three canyon streets at a scale of 1:5. Four (4) continuous parallel buildings made of containers were used to establish the street canyons. The scale of 1:5 was based on the stacking height of the containers. The W/H (Width/Height) ratio has been retained to 0.4. The three streets had the same width: 2 m, height: 5.2 m and length: 18.2 m. The

Fig. 3 Daily NOx (ppbv) variation in the pilot canyon



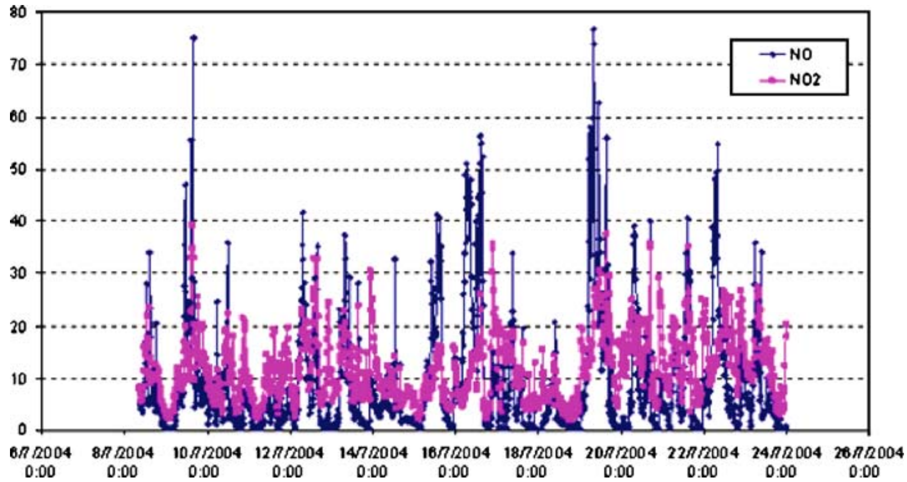


Fig. 4 Daily NO and NO_2 (ppbv) variation in the TiO_2 pilot canyon (Right wall)

orientation of the axis of the street was 52.24° compared to the northern section. (Fig. 1)

The walls surface of the second in the series of the three consecutive ones – canyon street was covered with TiO_2 treated material panels. The material was a mix mortar for external covering produced by Italcementi Group, based on mineral binder treated with 3% TiO_2 and sand. The walls of the first canyon were bare while the walls of the third were covered with non-TiO_2 treated mortar panels (Reference Street). Streets floor were treated with a 2-layer protection coating with tar emulsion and gravels (Fig. 2)

In situ instrumentation

A gas emission source connected to a 19 m, closed-end, perforated, pipe distributor was installed in the middle, along the tested canyon. The number of holes and their diameter were suitably selected to achieve uniform distribution of gas emission. The length of the tube and the internal diameter was 19.2 m and 50 mm respectively (Fig. 2). Fourteen (14) holes with 5 mm diameter were drilled along the pipe. Two (2) holes with 12 mm diameter were drilled in the forepart and in the middle of the pipe for gas composition and velocity measurements purposes. NOx, SO_2, CO, CO_2 were measured in the middle hole of the source pipe using a HORIBA PG-250 portable gas analyzer while benzene and TVOCs were measured with a Perkin Elmer Photovac portable Gas Chromatograph (Photo Ionization Detector). Gas velocity was measured in both forepart and middle hole using a FLOWTEST TCR TECORA flowmeter. The same instrument was used for temperature measurements in each hole of the pipe.

Continuous NOx measurements were performed on both sides of TiO_2 – treated and reference canyon in the middle axis using AC32M Environment s.a NOx chemiluminescence's analyzers. Background NOx and O_3 measurements took place on the top of an upper container using an API 200A Teledyne NOx chemiluminescence's analyzer and an O341M Environment s.a O_3 analyzer respectively. Meteorological parameters such as Wind Direction (WD), Wind

Table 1 Statistical evaluation of pollution source inorganic gas concentrations

	NO (ppm)	NOx (ppm)	SO_2 (ppm)	CO (ppm)	CO_2 (%vol)	O_2 (% vol)	C_6H_6/ ppm	TVOC/ ppc
Average	3.49	3.49	26.1	over	0.37	17.9	9.07	234
Min	0.60	0.70	4.60	over	0.18	17.0	1.85	102
Max	10.6	10.5	64.0	over	0.89	18.9	17.0	521
Median	1.90	200	23.0	over	0.34	17.9	9.40	202
Stolv	291	287	14.9		0.15	0.35	3.77	89.0
Counts	55	54	55		55	55	53	54

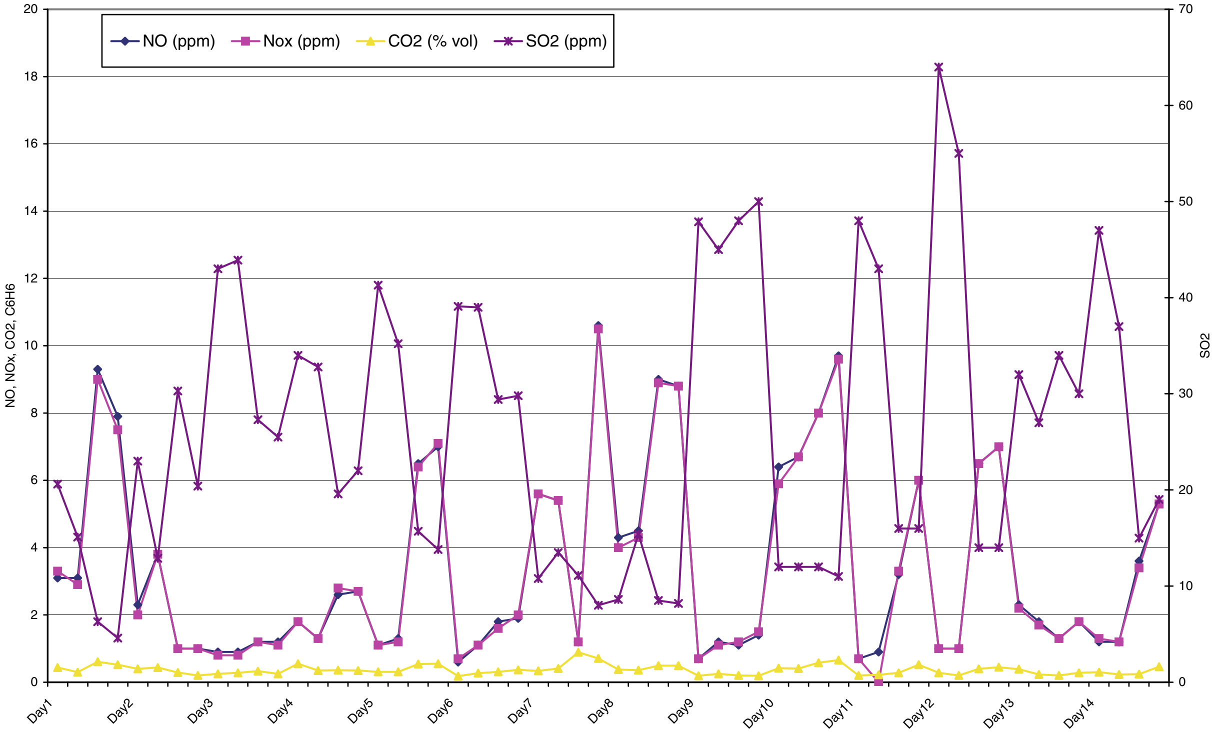


Fig. 5 Pollution source inorganic pollutants variation

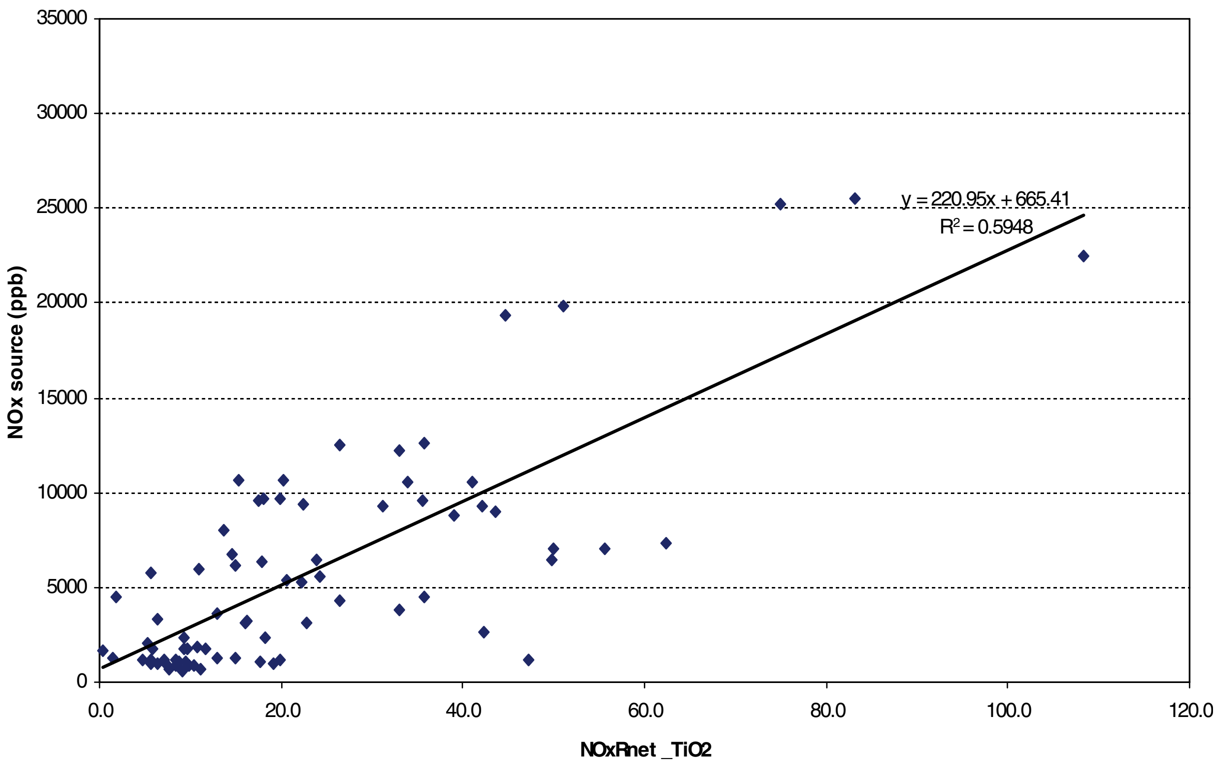


Fig. 6 Correlation between NOx source and NOx values measured on the Right wall

Speed (WS), Temperature (T), Relative Humidity (RH) and solar irradiation were recorded continuously with the use of meteorological masts placed in three different sites around the pilot site. Three meters, 5 m and 10 m masts were placed on the top of an upper container, westerly and southerly of the canyon respectively. Calibration of all instruments was performed on site and according to a calibration and maintenance protocol.

Duration

The measurement campaign took place during the period between the 9th July and the 3rd of September 2004. Meteorological conditions in that region during this period are usually characterised by high solar intensities and low wind-speeds. The experimental period could be divided into two sub-periods. From the 9th of July to the 23rd of August when the pollution source was placed into the TiO_2 canyon (central) and from the 23rd of August to 3rd of September when the source pipe was inside the reference canyon. In order to test both canyons under the same conditions, the geometry of the experimental site was changed during the second period by moving south the northern building. Then the new central canyon was the reference one. The engine working hours were set between 9:00 and 16:00. The engine operated for 14 days during the first period and for 6 days during the second period.

Results and discussion

Evaluation of pollution source impact

The effect of pollution source on NOx concentration inside the canyon is shown in Fig. 3. During the engine working hours (9:00–16:00) the in-canyon NOx values were significantly higher than during the rest of the day, reaching values between 10 up to 150 ppbv. When the engine works, NO is the dominant compound in the canyon street while during the engine off the NO and NO_2 values are following the background variation (Fig. 4).

Exhaust gas chemical composition was measured during the experiment in the middle hole of the

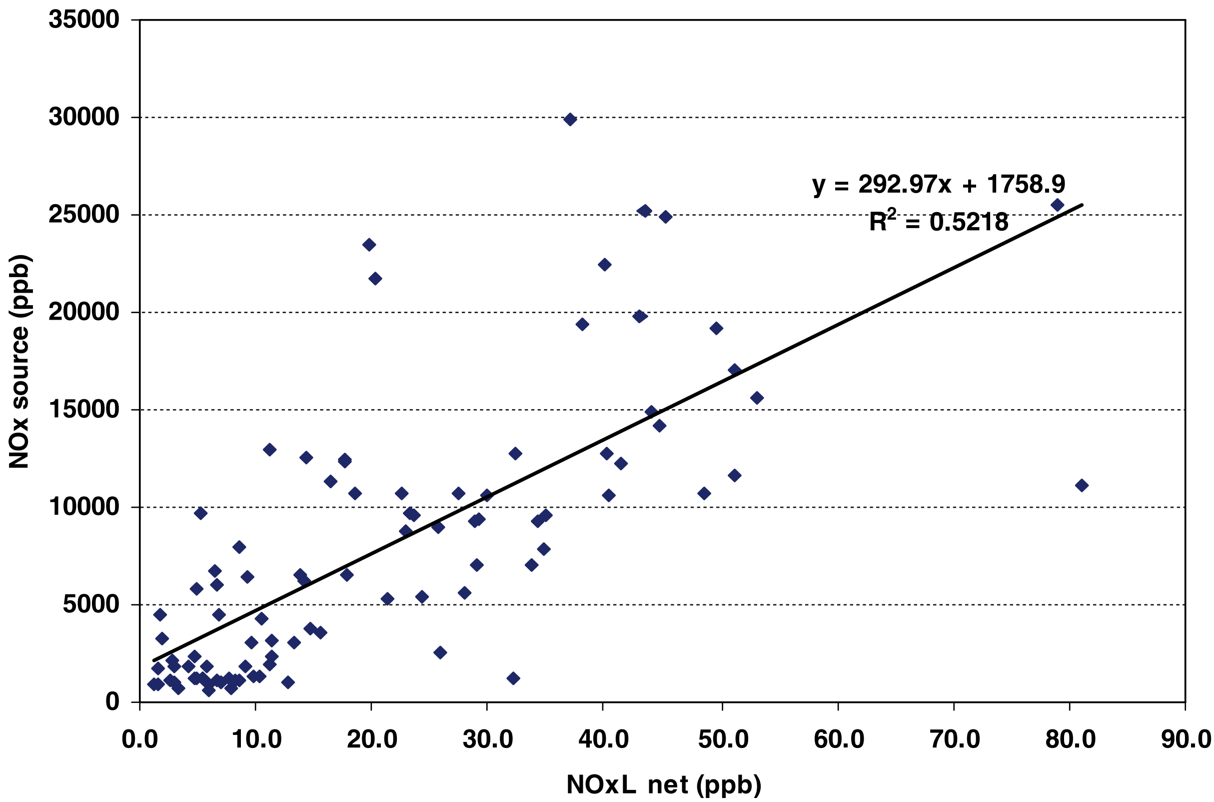


Fig. 7 Correlation between NOx source and NOx values measured on the Left wall

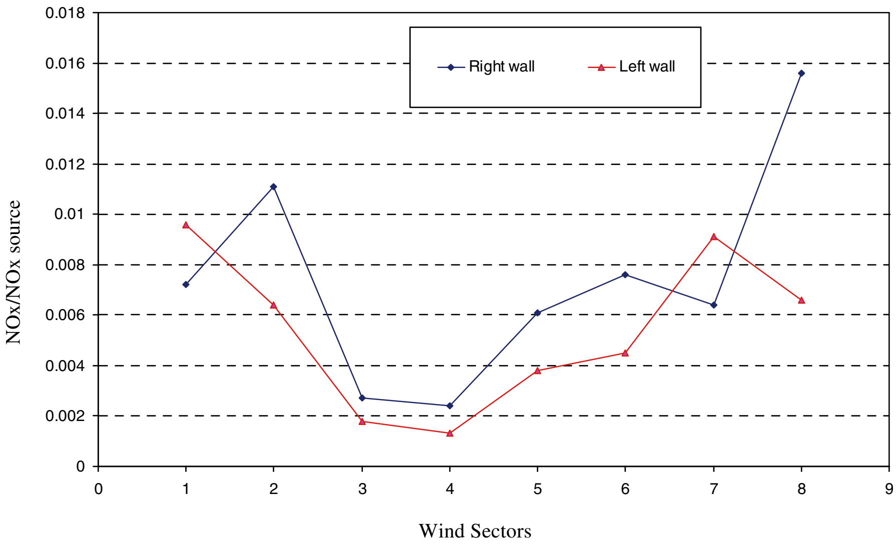


Fig. 8 NOxR/NOx source and NOxL/NOx source vs WD

perforated pipe. Table 1 presents a statistical evaluation of the measured pollution source data. Since NOx source emission was not stable (Fig. 5), affected the concentration of NOx inside the same canyon. The NOx concentrations measured on the right wall of the canyon (NOxR) as well as on the left wall (NOxL) were roughly correlated with the emitted NOx (Figs. 6 and 7).

The concentration level of NOx was also related to meteorological parameters. Figure 8 shows that the NOxR/NOx source and NOxL/NOx source aspect ratio were higher when winds from the northern sector were prevailing. The effect of wind speed on NOx concentration is varied depending on the orientation of the wall and the WD. For example on sector 7 (West), NOxR concentration was negatively correlated with WS (Fig. 9), while at the same sector WS didn't seem to affect NOxL concentration level (Fig. 10).

Evaluation of TiO_2 treated material photocatalytic efficiency

Since the measurements in TiO_2 and reference canyon were performed during different time periods, possible changes caused by different meteorological conditions and local parameters (background values) could affect the results. Particular elaborations of the measurement values were performed in order to establish a reliable comparison between the measure-

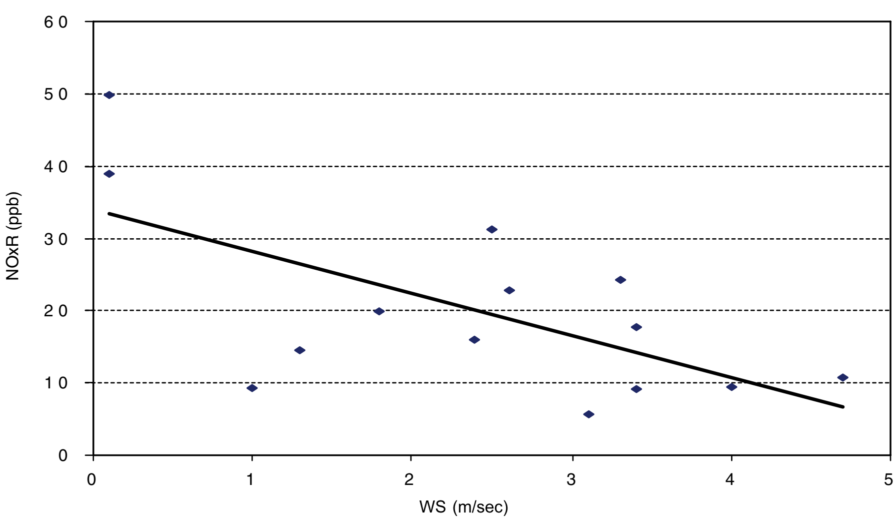


Fig. 9 NOxR concentration vs WS in sector 7 (West)

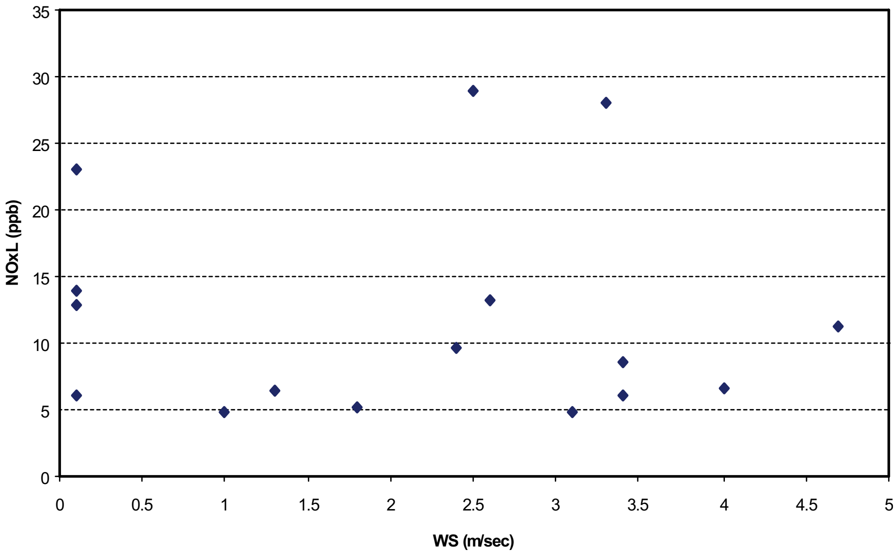


Fig. 10 NOxL concentration vs WS in sector 7 (West)

ments of the two periods. NOx background values were subtracted from the corresponding inside canyon NOx values for all the periods that the engine worked. So only net NOx values (come from the artificial source) took part in the calculations avoiding background differences between the two periods to affect the results. Table 2 presents a statistical evaluation of the background inorganic pollutants values. NOx concentrations were evaluated per wind sector so that differences in wind directions could not affect the comparison between the two periods.

The difference of the pollution level between the TiO_2 treated canyon and the reference one indicate the efficiency of the photocatalytic material to remove NOx under normal environmental conditions. Figures 11 and 12 show the significantly higher NOx levels, which were observed in the reference canyon. Depending on the wind sector, the NOx concentration in TiO_2 canyon (right wall) presented 41.2 up to 82% lower variation than the one observed in the reference canyon for the same conditions. The corresponding percentages for the left wall varied between 36.7 and 75.1%.

Table 2 Statistical evaluation of background inorganic gas concentrations (ppbv)

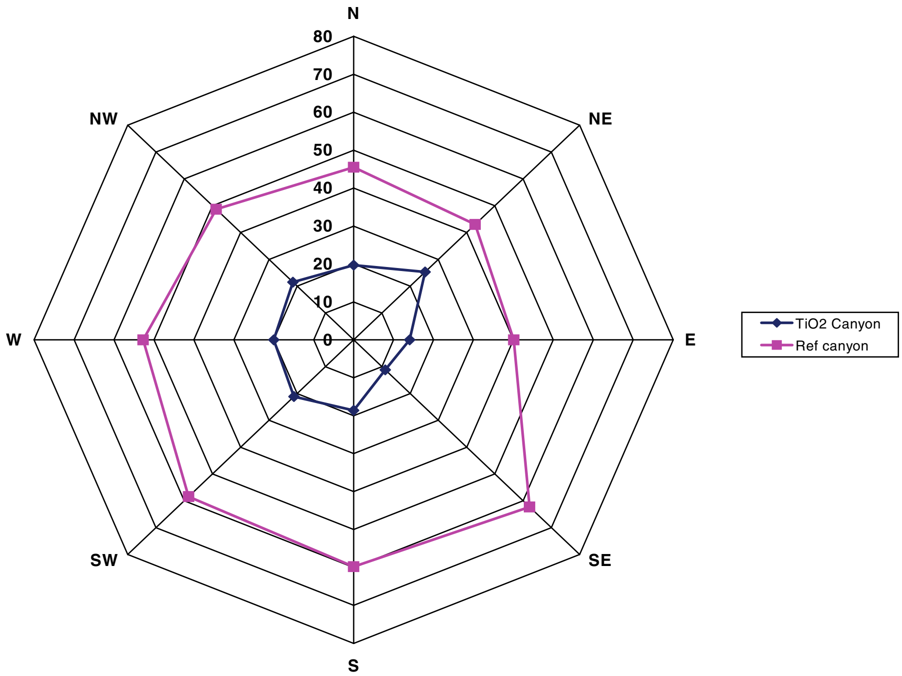
	NO	NO_2	O_3
Average	7.25	10.0	29.5
Min	0.10	0.10	0.10
Max	73.2	59.3	94.1
Median	4.00	7.50	23.6
Stdv	9.91	8.70	22.3

The depollution effectiveness of the TiO_2-material was confirmed by the aid of model simulations. The three-dimensional microscale model MIMO was used to simulate the configuration of the field experiment (Moussiopoulos et al. 2005). The experimental NOx measurements were compared with the numerical simulation results for both walls. The comparison shows that model results are in a very good agreement with the in situ measurements, verifying the photocatalytical efficiency of the material.

Conclusions

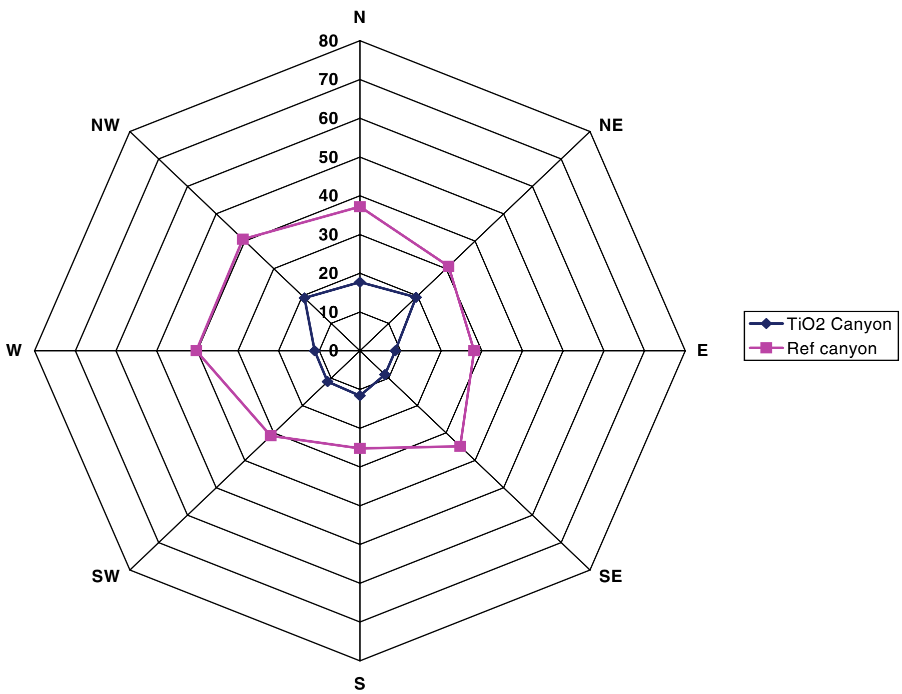
Three artificial canyon streets were constructed in CTG cement plant in France. The purpose of the construction was to estimate the photocatalytic efficiency of a TiO_2-containing mortar. The pilot site had special geometrical features and involved specific instrumentation in order to perform a reliable comparison between the TiO_2 and reference canyon NOx measurements. The difference between the NOx levels in the canyons indicated the significant ability of TiO_2 treated mortar to remove NOx from ambient air. NOx recorded concentrations in TiO_2 canyon were 36.7–82.0% lower than the ones observed in the reference one. The above percentage was varied due to differences on pollution source emissions, wind

Fig. 11 NOx mean concentration (ppb) per sector in TiO_2 and reference canyon on right wall



direction and the orientation of the wall. Comparison between experimental results and numerical simulations were in a very good agreement, verifying the photocatalytic effectiveness of the material. The dilution factor between the source and the receptor points were strongly correlated with wind direction. The right wall concentrations in most of the cases were higher than the ones on the left wall in both canyons. Wind speed effect seemed to depend on walls orientation and wind direction, while the solar irradiation between the two periods was not significant to affect results.

Fig. 12 NOx mean concentration (ppb) per sector in TiO_2 and reference canyon on left wall



Based on the results of the present work, further studies could be conducted in order to evaluate the impact of photocatalytic coverings on the NOx levels in an urban street canyon.

Acknowledgements This work took place in the frame of PICADA project funded by EU (GRD1-2001-40449).

References

Agrios, A. G., & Pichat, P. (2005). An overview of the state of the art and perspectives on materials and applications of photocatalysis over TiO_2. *Journal of Applied Electrochemistry, 35*, 655–663.

Ao, C. H., Lee, S. C., Mak, C. L., & Chan, L. Y. (2003). Photodegradation of VOCs and NO for indoor purification using TiO_2: promotion versus inhibition effect of NO. *Applied Catalysis B, Environmental, 42*, 119–129.

Blake, D. M. (2001). Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air. National Renewable Energy Laboratory, from http://www.osti.gov/bridge.

Dalton, J. S., Janes, P. A., Jones, N. G., Nicholson, J. A., Hallam, K. R., & Allen, G. C. (2002). Photocatalytic oxidation of Nox gases using TiO2: A surface spectroscopic approach. *Environmental Pollution, 120*, 415–422.

Fujishima, A., Hashimoto, K., & Watanabe, T. (1999). *TiO_2 photocatalysis: Fundamentals and applications*. Japan: BKC, Inc.

Ibrahim, H., & Lasa, H. (2002). Photocatalytic conversion of air borne pollutants effect of catalyst type loading in a novel photo-CREC-air unit. *Applied Catalysis. B, Environmental, 38*, 201–213.

Kaneko, M., & Okura, I. (2002). Photocatalysis science and technology. In *Cleaning Atmospheric Environment* (pp. 123–155). Tokyo: Kodansha.

Lewandowski, M., & Ollis, D. F. (2004). Photocatalytic oxidation of gas phase aromatic pollutants. In V. Ramamurthy, K. S. Schanze (Eds.), *Seminoconductor photochemistry and photophysics* (pp. 249–282). New York: Marcel Dekker.

Moussiopoulos, N., Ossanlis, I., Barbas, Ph., & Bartzis, J. (2005). *Comparison of numerical and experimental results for the evaluation of the depollution effectiveness of photocatalytic coverings in street canyons'* Paper presented at the 5th International Conference on Urban Air Quality, Valencia, Spain, p.68.

Pichat, P. (2003). Photocatalytic degradation of pollutants in water and air: Basic concepts and applications. In M. A. Tarr (Ed.), *Chemical degradation methods for wastes and pollutants: Environmental and industrial applications* (pp. 77–119). New York: Marcel Dekker.

Pichat, P., Disdier, J., Hoang-Van, C., Mas, D., Goutailler, G., & Gaysse, C. (2000). Purification/deodorization of indoor air and gaseous effluents by TiO_2 photocatalysis. *Catalysis Today, 63*, 363–369.

Strini, A., Cassese, S., & Schiavi, L. (2005). Measurement of benzene, toluene, ethylbenzene and *o*-xylene gas phase photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor. *Applied Catalysis B, Environmental, 61*, 90–97.

Zhang, J., Terukazu, A., Minagawa, M., Kinugawa, K., Yamashita, H., Matsuoka, M., Anpo, M. (2001). Investigations of TiO2 Photocatalysts for the decomposition of NO in the Flow System. *Journal of Catalysis, 198*, 1–8.