

## Results action P1 - Laboratory testing of photocatalytic material

The main objective of action P1 was to provide a complete chemical characterization of the gas phase products and the runoff samples as well as an identification of new chemical reactions on photocatalytic urban surface films by laboratory experiments. Partners involved are the CNRS-IRCELYON, the BUW at Wuppertal as well as TROPOS at Leipzig (formerly IfT, coordinating action P1). In action P1 the effectiveness and influence of photocatalytic material under controlled conditions should be characterized on different atmospheric processes on the laboratory scale. Commercial photocatalytic materials were studied for their catalytic activity and on the product formation in the reaction of nitrogen oxides ( $\text{NO}_x$ ), gas phase nitrous acid (HONO), formaldehyde (HCHO) and other selected volatile organic compounds (VOCs) by using similar experimental setups based on small gas flow reactors. To investigate the photocatalytic mortar surfaces used in the implementation actions I1 and I2, glass plates were coated with a resulting surface thickness of about 2-4 mm. An overview about the experimental setup and the types of reactors including the coated glass plate is shown in Fig. 1.

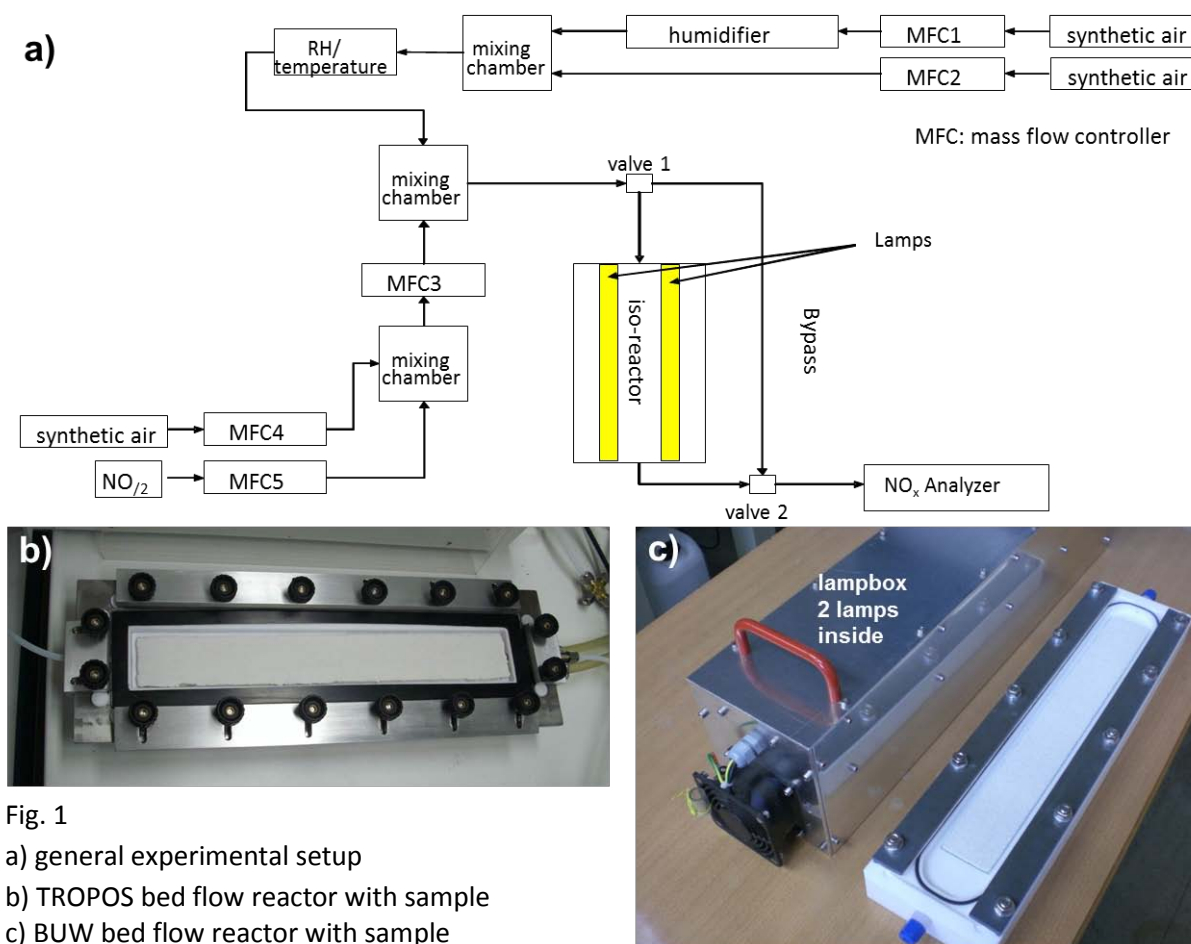


Fig. 1

- a) general experimental setup
- b) TROPOS bed flow reactor with sample
- c) BUW bed flow reactor with sample

In general, each experiment started by measuring under “Bypass” conditions, for which the gas phase analytes are not in contact with the reactor and the photocatalytic material. After adjustment of the starting experimental conditions (e.g., mixing ratio, flow rate and relative humidity) the gas passes the reactor with lights off to study the dark reaction of the target analytes with the active surface. Following

this step, the lights were switched on to observe the photocatalytic effect of the applied material for the adjusted specific conditions.

Due to the increasing relevance of  $\text{NO}_x$  for urban air quality, especially at traffic hot spots, the main focus in action P1 was to study the photocatalytic depollution effect of the material for nitrogen monoxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ). Experiments with pure NO,  $\text{NO}_2$  and mixtures in synthetic air were performed under variable experimental conditions such as initial mixing ratio, relative humidity (RH), flow rate and light intensity. Two experiments with pure NO and  $\text{NO}_2$  mixed with synthetic air are shown in Fig. 2.

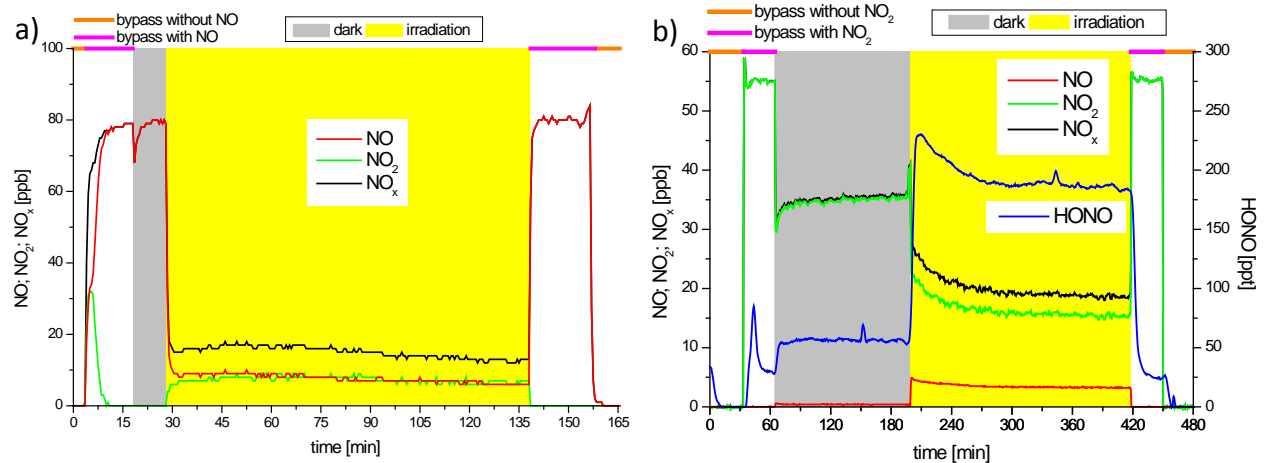


Fig. 2: a) NO-experiment: 3.0 L/min flow; RH50%

b) NO<sub>2</sub>-experiment: 3.0 L/min flow; RH50%

The experiment with pure NO in synthetic air (Fig. 2a) showed no significant dark reaction for NO with the applied photocatalytic material, but a strong photocatalytic decomposition of NO when the lights were switched on. This result proves the ability of the material to depollute air contaminated with NO under these experimental conditions. In contrast to NO,  $\text{NO}_2$  showed a significant dark reaction, but a significantly lower photocatalytic (see green line Fig. 2b). However, this also underlines the ability of the coating to degrade  $\text{NO}_2$ . The observed formation of HONO (0.5%) during this experiment can be neglected, due to blank experiments resulting in a formation of 1%. This was confirmed in experiments with pure HONO mixtures, for which strong adsorption of HONO was observed under all experimental conditions. Based on these types of experiments, a first order rate constant was determined which was used to calculate the dimensionless uptake coefficient  $\gamma$  for each target analyte. The uptake coefficient describes the rate of reactive collisions divided by the rate of all collisions of a molecule with a surface (equation 1).

$$\gamma_{(x+\text{TiO}_2)} = \frac{4 \cdot k_{(x+\text{TiO}_2)} \cdot S}{\langle c \rangle_{(x)} \cdot V} \quad \begin{array}{l} k: \text{first order rate constant;} \\ V: \text{reactor volume} \end{array} \quad \begin{array}{l} \langle c \rangle: \text{average molecule velocity} \\ S: \text{active surface} \end{array} \quad (1)$$

The calculated uptake coefficient for NO (dark) is about  $10^{-7}$  and increases up to  $10^{-5}$  under light conditions. Due to the stronger dark reaction of  $\text{NO}_2$  the uptake coefficient for  $\text{NO}_2$  (dark) is already in the range of  $10^{-5}$  and is not increasing under light conditions as much as it is observed for NO. Nevertheless, the overall uptake coefficient under light conditions is almost similar for NO and  $\text{NO}_2$ . To

further characterize the photocatalytic material, the influence of different experimental conditions on the resulting uptake coefficient was studied. An overview about the outcome for NO and NO<sub>2</sub> is illustrated in Fig. 3.

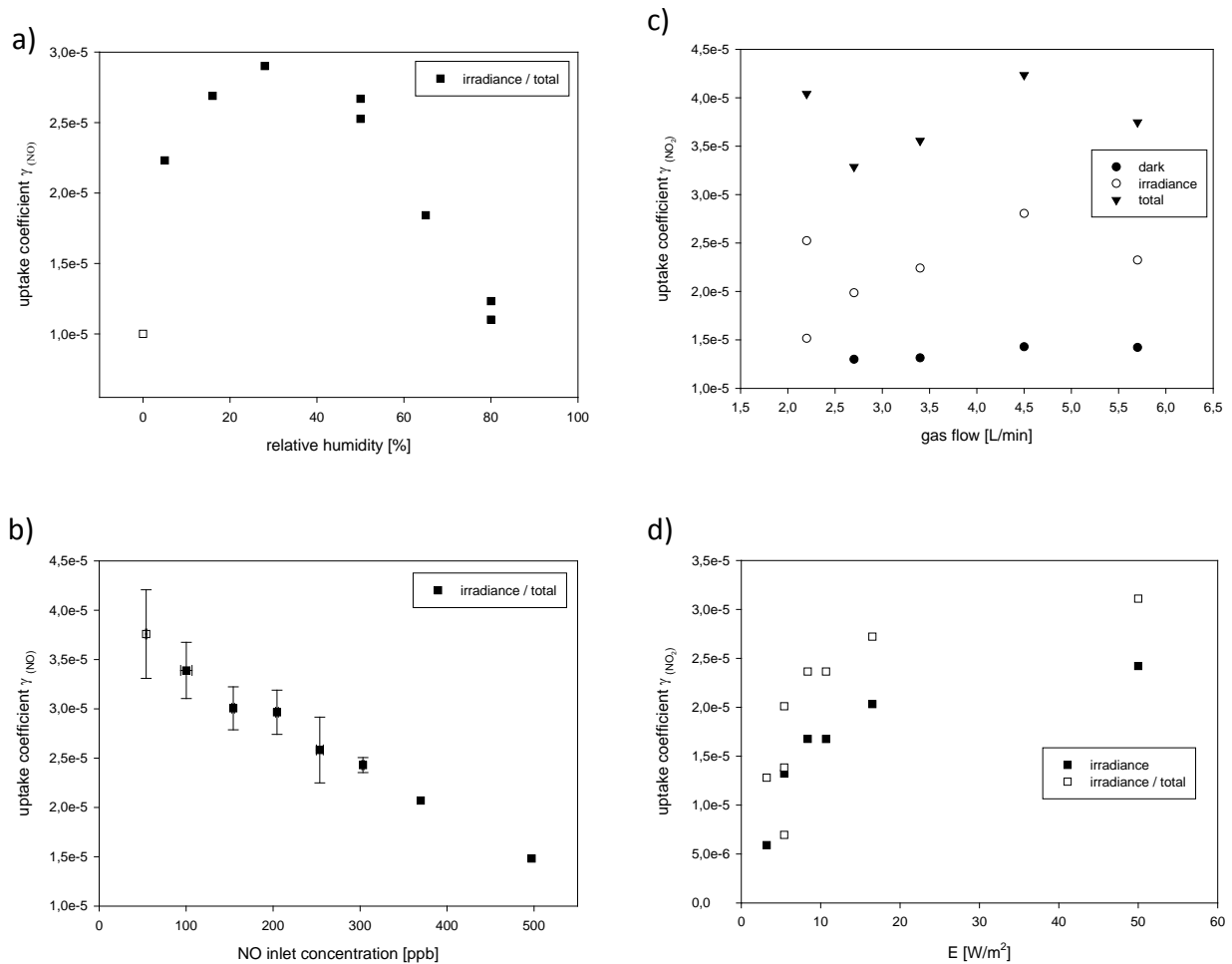


Fig. 3: Bed flow reactor experiments with NO and NO<sub>2</sub> under variation of experimental conditions

a) NO-exp.: 3 L/min flow,  $c(NO)=100$  ppb

c) NO<sub>2</sub>-exp.: RH 50%,  $c(NO_2)=55$  ppb

b) NO-exp.: 3 L/min flow, RH 50%

d) NO<sub>2</sub>-exp.: 3.3 L/min flow, RH 50%,  $c(NO_2)=85$  ppb

The uptake coefficient for NO showed a clear dependence on RH (Fig. 3a). The highest uptake coefficient was observed at RH 25-30%, whereas at low (less reactive radicals formed) and high RH values (competition between the water molecules and NO for the active sites on the surface) the uptake coefficient decreases significantly. Furthermore, a continuously decreasing uptake coefficient of NO was observed with increasing NO concentration in Fig. 3b. This demonstrates that the NO kinetics is already  $<1$  at atmospheric relevant concentration, which is explained by saturation of active sites according to the Langmuir-Hinshelwood mechanism. Fig. 3c illustrates that both the dark and the photocatalytic reaction of NO<sub>2</sub> is independent on the flow rate, which indicates no diffusion limitation in the reaction system. Light intensity is of course a very important parameter for photocatalytic reactions. The dependence of the NO<sub>2</sub> reaction on the amount of irradiance level is shown in Fig. 3d. An almost linear

dependence was only seen for values up to  $8 \text{ W/m}^2$ , after that the dependence became non-linear, which levels off at irradiance values higher than  $20 \text{ W/m}^2$ .

Beside the kinetic studies also the formation of reaction products on the photocatalytic surface was investigated. For example after experiments with  $\text{NO}_2$ , the surface was eluted with distilled water and the solution subsequently analyzed via ion chromatography. Nitrate ( $\text{NO}_3^-$ ) was determined as the major reaction product with a yield of  $72 \pm 8\%$ . In addition, also a significant nitrite ( $\text{NO}_2^-$ ) yield of  $22 \pm 5\%$  was observed. This result can be very well explained by the alkaline surface properties of the investigated photocatalytic coating, where adsorbed nitrite is obviously not photocatalytically oxidized. Experiments with gas phase nitrous acid ( $\text{HONO}$ ) showed only a strong dark uptake ( $v_{\text{dark}} \sim 10^{-5}$ ) but no photocatalytic uptake of  $\text{HONO}$  was observed, which confirms the result by ion chromatography. However, if the surface is not washed, e.g. by rain, it is important to notice that both adsorbed nitrate and nitrite can lead to a formation of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{HONO}$  under irradiation (renoxification process).

Beside  $\text{NO}_x$  also the behavior of  $\text{HCHO}$  and other selected VOCs on the identical type of photocatalytic coating was tested. The experimental results for  $\text{HCHO}$  are shown in Fig. 4.

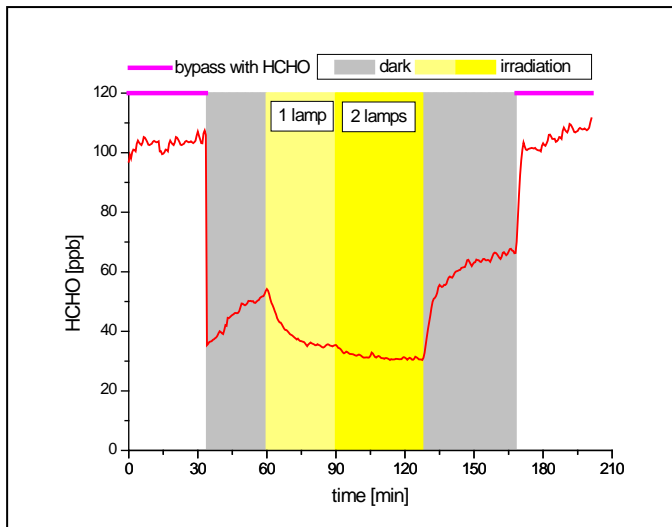


Fig. 4:

Bed flow reactor experiment with  $\text{HCHO}$ ,  $\text{RH}50\%$ ,

1 lamp:  $24.5 \text{ W/m}^2$ ,

2 lamps:  $49.5 \text{ W/m}^2$

For  $\text{HCHO}$ , a strong dark uptake ( $9.9 \cdot 10^{-6}$ ) followed by a small light reaction (approx.  $1.3 \cdot 10^{-5}$ ) was observed for the photocatalytic coating. When similar non photoactive samples were used, only dark uptake was observed, confirming a photocatalytic reaction of  $\text{HCHO}$ . However, at atmospheric relevant low  $\text{HCHO}$  concentrations,  $\text{HCHO}$  was photocatalytically formed on the mortar surfaces, which is in excellent agreement with the tunnel and street canyon results where clear formation was observed under irradiation (see actions I1 and I2). Furthermore different VOCs (toluene, benzene, different partially halogenated VOCs) were studied for their photocatalytic oxidation and product formation (e.g.  $\text{HCHO}$ ,  $\text{CO}_2$ , VOCs) on the mortar surfaces. However, for none of the tested VOCs any photocatalytic reactivity or product formation was observed using the photocatalytic coatings used in the implementation actions (data not shown).

The presented laboratory results on a photocatalytic active mortar coating and also additional comparable studies using other active surfaces in action P1 were important for both the preparation and duration of the field measurement campaigns as well as to provide input data for the final model calculations in the PhotoPaq-project.