AN INDOOR AIR QUALITY MODEL TO TEST THE DEPOLLUTION EFFICIENCY OF INDOOR SURFACES CONTAINING NANOPARTICLES

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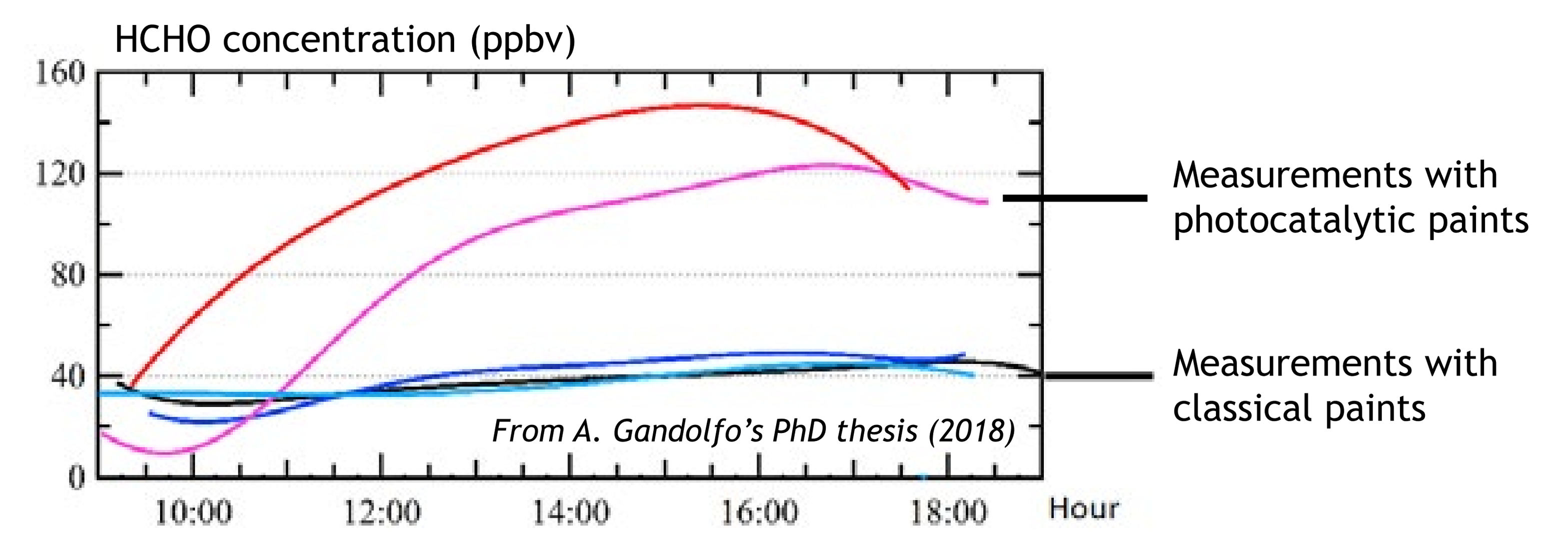
Serenade — Safe(r) Ecodesign Research and Education applied to NAnomaterial DEvelopment.

1. Motivation

Context : Development of paints containing TiO_2 nanoparticles (NPs) as a means to improve indoor air quality (IAQ). The photo-activated TiO_2 NPs produce OH radicals that can degrade volatile organic compounds (VOCs).

Problematic : Measurements performed in a room whose walls were covered by such paints, revealed a completely opposite effect, with a strong increase of pollution level.

Aim : Developping a numerical model allowing to simulate indoor concentrations to understand and assess the effect of these photocatalytic paints on IAQ.



2. Presentation of the H²I model

The H²I (Homogeneous Heterogeneous Indoor) model is a **two-box model** allowing to differenciate the volume illuminated by the direct light of the sun (denoted L), and the volume illuminated by indirect light (denoted L). The time evolution of the concentrations in the boxes is defined as :

$$\frac{dC_i^L}{dt} = k_{AER}(fC_i^{Out} - C_i^L) - k^L_{DEP,i}C_i^L + k^L_{BOX}(-C_i^L + C_i^S) + \frac{Q_{room,i}}{V_{room}} + \frac{E^L_{paint,i}S^L_{paint,i}}{V^L_{box}} + \sum_q \frac{R^j_{iq}}{V^L_{box}}$$

$$\frac{dC_i^S}{dt} = \underbrace{k_{AER}(fC_i^{Out} - C_i^S)}_{\text{Exchanges between the room and its outside}} - \underbrace{k^S_{DEP,i}C_i^S}_{\text{Deposition}} + \underbrace{k^S_{BOX}(C_i^L - C_i^S)}_{\text{Exchanges between the boxes}} + \underbrace{\frac{Q_{room,i}}{V_{room}} + \frac{E^S_{paint,i}S^S_{paint,i}}{V^S_{box}}}_{\text{Room and paints emissions}} + \underbrace{\sum_q \frac{R^j_{iq}}{V^S_{box}}}_{\text{Chemical reactivity}}$$

- t : time [s]
- $C_i^{L,S}$: concentration of species i in box L,S [$\mu g.m^{-3}$]
- C_i^{Out} : outdoor concentration of species i [$\mu g.m^{-3}$]
- f : building filtration factor [-]
- k_{AER} : air exchange rate between the room and its outside [s^{-1}]
- $k_{DEP,i}$: deposition rate of species i [s^{-1}]
- k_{BOX} : air exchange rate between the boxes [s^{-1}]
- V_{room} : total volume of the room [m^3]
- $V_{box}^{L,S}$: volume of box L,S [m^3]
- $Q_{room,i}$: room emission rate of species i [$\mu g.s^{-1}$]
- $S_{paint,i}^{L,S}$: surface of paint in box L,S [m^2]
- $E_{paint,i}^{L,S}$: paint emission rate of species i in box L,S [$\mu g.m^{-2}.s^{-1}$]
- R_{iq} : mass reaction rate between species i and species q [$\mu g.s^{-1}$]

3. Heterogeneous reactivity

Organic and inorganic species can sorb on surfaces at a rate k_{DEP} defined as :

$$\frac{1}{k^j_{DEP,i}} = \frac{1}{k^j_{tran,i}} + \frac{1}{k^j_{react,i}}$$

- $v_{trd,i}$: deposition velocity of species i [$m.s^{-1}$] (depends on the speed of air mixing)
- γ_i : uptake coefficient of species i [-]
- ω_i : thermal velocity of species i [$m.s^{-1}$]
- j : box indicator (L or S)
- S_{box}^j : box solid surface [m^2]

$$k^j_{tran,i} = v_{trd,i}\frac{S^j_{box}}{V^j_{box}} \qquad k^j_{react,i} = \frac{\gamma_i \omega_i}{4}\frac{S^j_{box}}{V^j_{box}}$$

Transport to surfaces — Efficiency of collisions with surfaces

Once sorbed, the organic and some inorganic species like ozone are assumed to stay adsorbed or to be degraded by the photocatalyst. The NOy compounds (NO, NO_2, HONO) have the possibility to react thanks to the introduction of sorbed compounds $NO_{(ad)}$, $NO_{2(ad)}$, $HONO_{(ad)}$, $HNO_{3(ad)}$:

- $NO_{2(ad)}$ (+ 0.5 H_2O) → 0.5 $HONO_{(ad)}$ + 0.5 $HNO_{3(ad)}$
- $HNO_{3(ad)}$ + $HONO_{(ad)}$ → 2 $NO_{(ad)}$ (+ H_2O + O_2)
- $HONO_{(ad)}$ → 0.5 $NO_{(ad)}$ + 0.5 $NO_{2(ad)}$ (+ 0.5 H_2O)
- $NO_{(ad)}$ + $HNO_{3(ad)}$ → $NO_{2(ad)}$ + $HONO_{(ad)}$

New in IAQ model (last three reactions)

Finally, the NOy compounds can desorb at a rate $k_{i,(ad)} = k'_{i,(ad)}\, n_{H_2O}$ where n_{H_2O} is the number of water molecules computed from absolute humidity.

4. Input data and model parameters

Input data :

- Room temperature and relative humidity
- Evolution of the volumes and surfaces of the boxes
- Photolysis constants for both boxes
- VOCs, NO, NO_2 and O_3 outdoor concentrations
- VOCs, NOy and O_3 initial indoor concentrations
- NO_2 uptake coefficient + parameterization with temperature and humidity
- Ventilation rate k_{AER}

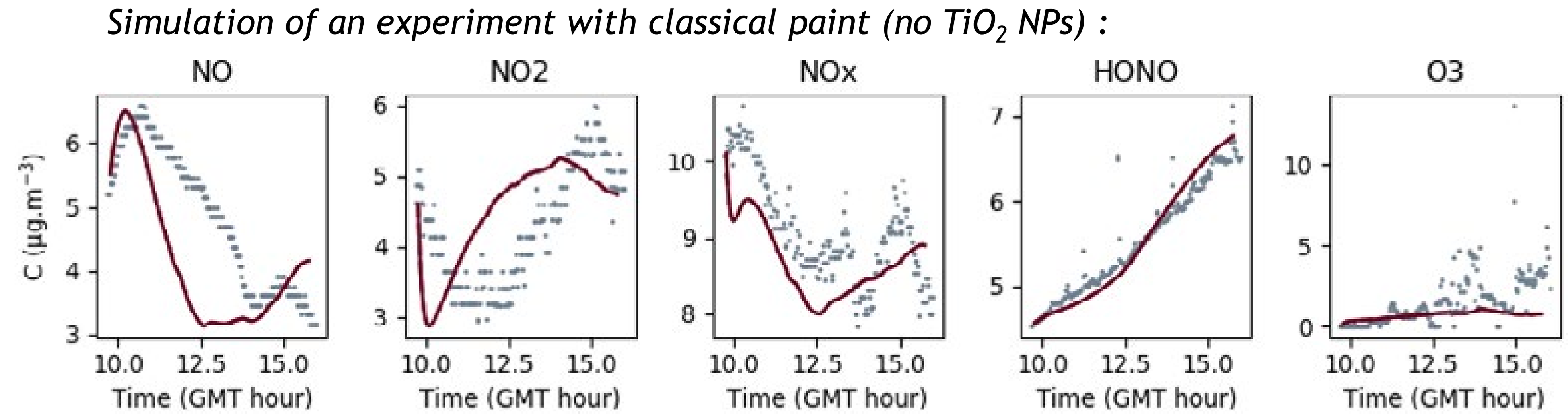
Model parameters :

- Building filtration factor and average speed of air in the room
- NO, HONO and O_3 uptake coefficients γ_i
- NO, NO_2 and HONO evaporation constants $k'_{i,(ad)}$
- Stoichiometry of the NO_2 heterogeneous hydrolysis : $NO_{2(ad)} \rightarrow B_{HNO_3}\, HNO_{3(ad)} + B_{HONO}\, HONO_{(ad)}$
- Kinetic rates of the surface reactions

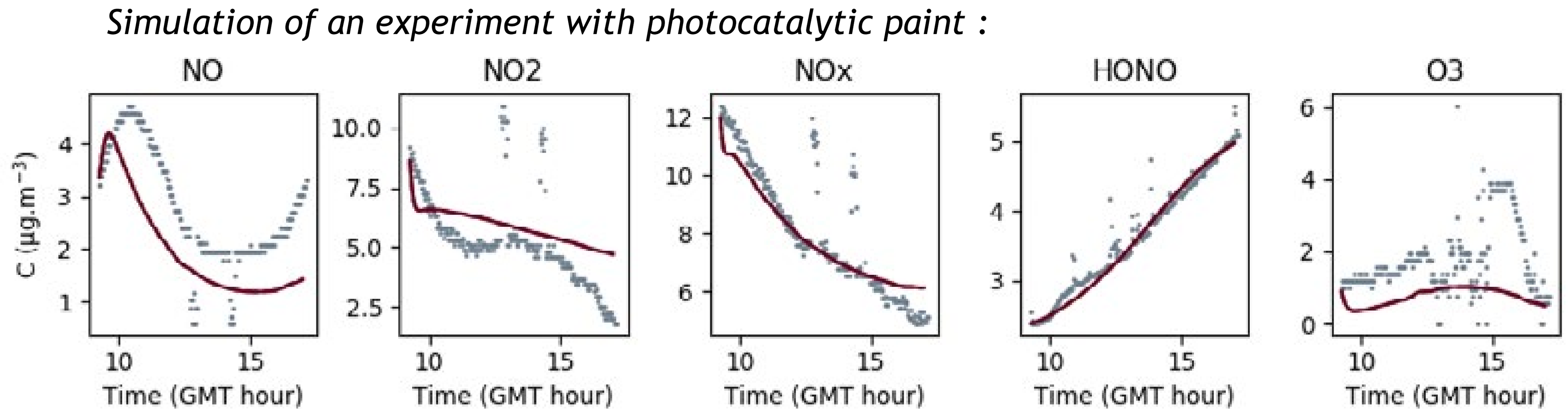
5. Simulations of the experiments

The simulations are performed by constraining the organic compounds to their measured values. The model parameters are adapted to achieve the least error as possible between data (grey curve) and model (red curve), for the four measured inorganic species (NO, NO_2, HONO, O_3). The model parameters share the same values for the three simulated experiments, apart from the desorption constants.

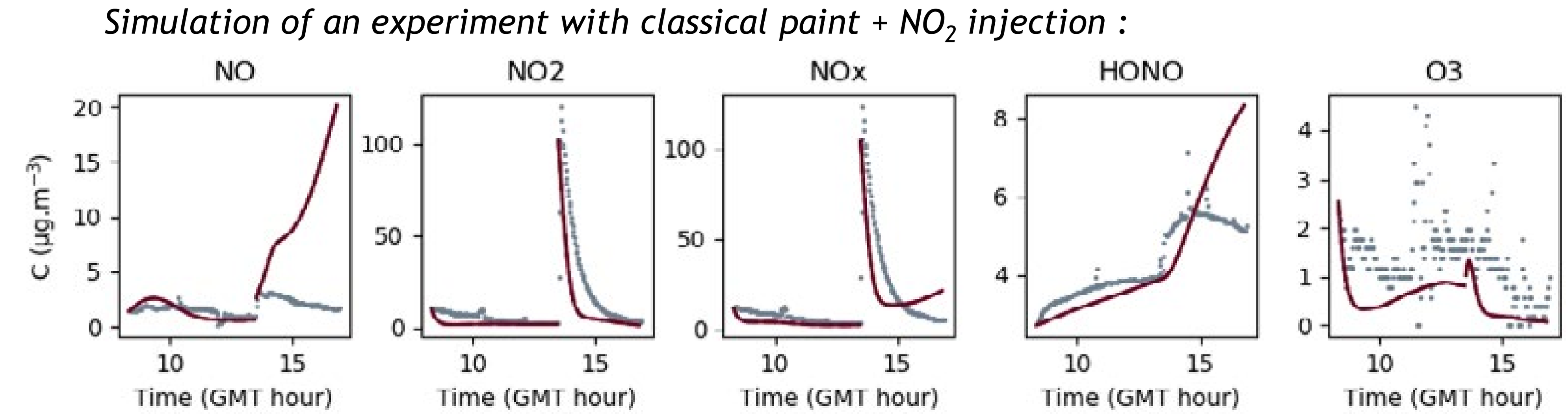
Simulation of an experiment with classical paint (no TiO_2 NPs) :



Simulation of an experiment with photocatalytic paint :



Simulation of an experiment with classical paint + NO_2 injection :



Satisfying results are achieved for the four inorganic compounds, unless in the experiment with NO_2 injection, which calls for a more complexe parameterization of desorption. We can note that the type of paint does not influence the modelled/measured inorganic concentrations.

6. Conclusion

The H²I model has been developped to simulate the chemistry of inorganic compounds in indoor environments. It can now be further developped to simulate the organic compounds concentrations using the paint emission rates determined in reactor experiments. In the future, such developement should allow to assess the depollution efficiency of other NPs-bearing paint characterized experimentally, without the necessity to perform an indoor campaign.

Reference : *Eve-Agnès Fiorentino, Henri Wortham, and Karine Sartelet. Combining homogeneous and heterogeneous chemistry to model inorganic compounds concentrations in indoor environments: the H²I model (v1.0).* Geoscientic Model Development Discussions, *2020:1-58, 2020.* URL: https://gmd.copernicus.org/preprints/gmd-2020-300/