Geoscientific

Model Development

Discussions

Open Access

GMDD

Interactive

comment

Interactive comment on "Combining homogeneous and heterogeneous chemistry to model inorganic compounds concentrations in indoor environments: the H^{2}I model (v1.0)" *by* Eve-Agnès Fiorentino et al.

Anonymous Referee #1

Received and published: 15 February 2021

The manuscript entitled "Combining homogeneous and heterogeneous chemistry to model inorganic compounds concentrations in indoor environments: the H2I model (v1.0)" by Fiorentino et al. describes a chemical box model that has been developed for indoor environments. There are relatively few thorough indoor air models. The manuscript focuses on the inclusion of heterogeneous chemistry, which is extremely important for indoor air. The development of this model represents an important new tool for the study of indoor air chemistry. While this is not the first example of an indoor model that treats heterogeneous chemistry, it is nonetheless an important one.

Overall, the paper is dense and model description is extensive. It is recommended that the authors consider including a summary table of symbols used, as the notation can be difficult to follow.

The most important conceptual difference that this reviewer has with the paper is the treatment of surface chemistry. A prior study by Mendez et al (Indoor Air, 2017) worked within a similar conceptual framework to the present study and was not able to achieve strong agreement between the model and measurements in some cases, particularly when NO2 was high. A similar deficiency is found in the present model output. Other frameworks, like treating the surface as a multilayer reservoir that has a 'depth' (so to speak) has been suggested by other authors (Collins et al., Environ. Sci. Technol. 2018). Models may be more able to tolerate high concentrations of NO2 using equilibrium, rather than strict competitive adsorption kinetics (i.e. - surface site saturation). Stronger consideration of this issue appears to make an appearance in the Discussion section as a possibility for future study. Further investigation of the possibility that competitive adsorption/desorption may not represent indoor surface films is strongly recommended.

The paper should be acceptable in Geoscientific Model Development after consideration of these reviewer comments and a minor revision.

Specific Comments: Line 98-100: "the first two-box model allowing to consider the evolution of light intensity of each part along the day, as well as the volumes they occupy" Other partially illuminated models exist, including recent reports that use CFD for studies of HONO chemistry in partially illuminated spaces. It would be worthwhile to explicitly place the present model in a broader context.

Line 103: "acquired in Martigues" Please be more specific.

Line 138: "S_j_paint is the surface of paint in the box j [m-2]" The units suggest that this is a surface area-to-volume ratio, but the text suggests that it might be a surface area. Please clarify or correct.

Line 158-159: "The complement of S_L_box to obtain the surface of the volume V_L_box is the same as the complement of S_S_box..." This wording is very confusing. Perhaps clarifying "surface area" and referring to the 'box' rather than 'the volume' would help.

Broader comment: Referring to various forms of "S" parameters as 'surfaces' appears in many locations. Please be more specific about the type of quantity that "S" denotes.

Line 188-189: Similar efforts, but with ozone, have been made by Morrison et al. (Indoor Air, 2019). https://doi.org/10.1111/ina.12601

Line 248-249: "deposition of the OH radical is considered negligible compared to its consumption by reactivity" Is this statement made in reference to the heterogeneous reactivity of OH or the homogeneous gas phase reactivity? Indoor multiphase reactivity by OH has been shown by Alwarda et al (Indoor Air, 2018).

Section 2.5: Have the authors considered a distance dependence to actinic flux? Dependence of actinic flux on wavelength, distance, and other variables have been characterized by Zhou et al. (Indoor Air, 2021) and Kowal et al. (Environ. Sci. Technol., 2017).

Line 394-395: The definition of filtration factor here seems different than this reviewer's previous understanding. The filtration factor (or penetration factor, in Sarwar et al (2002)) describes the ability for a specific pollutant to penetrate the building envelope. It is not necessarily a measure of how airtight a building might be. It is related to the route and loss processes involved in transporting a particular pollutant from outdoors to indoors, and is independent of the air exchange rate (which is controlled in part by the airtight-ness of the building). NOx penetration factors have been measured by Zhao et al. (Environ. Sci. Technol., 2019; doi: 10.1021/acs.est.9b02920). These authors found that the NO penetration factor was ∼1 and for NO2 it was closer to 0.7 for the same environment. Please clarify and correct the text. Note: This reviewer clearly understands that perhaps filtration or penetration factors have not been determined

for the building being used in the present study, but citing values that are known for compounds in this study and that the filtration factor values are compound-specific are extremely important items for the reader to understand.

Line 393-395: This statement about competitive adsorption of H2O and HONO may not be relevant. Our current understanding of indoor surfaces includes the possibility that multilayers may exist. Please refer the overall comment on the treatment of surface chemistry at the top of this review.

Line 405-406: "no experimental validation of this production ratio is available" This is not true, as it has been a topic of research for many years. Most saliently, the group of Finlayson-Pitts has studied this concept, and the authors have cited several of their papers. In addition, Grassian and co-workers have studied this problem.

Section 5.1.2: Filtration factor – The description of the filtration factor is largely correct, but some of the description may confuse the meaning of the filtration factor.

Line 523: "outdoor pollutants like O3 and NO2". Why isn't NO in this list? NO mixing ratios outdoors are often greater than NO2 during daytime in cities when NO2 photolysis is rapid.

Line 533-534: Is it possible that the prevalence of Reaction S2 is overestimated?

Line 534: "As NO increases, NO2 increases by equilibration through homogeneous chemistry." This statement is unclear. It may be correct, but it is not clear enough to understand what it is supposed to mean.

Line 549-550: "The threshold value k_S1 = 0.003 s-1 is retained as it maximizes the NO2(ad) conversion." Why is this the most appropriate choice? Please further justify this decision. What impact does this decision have on other results?

Section 5.3.1: What happens if HONO and HNO3 dissociate?

Line 633: Please comment on how the uptake coefficient of HONO compares with the

literature.

Line 650-653: It is somewhat alarming to see that the parameters within the model must be altered in response to the reference experiments. The broader issue brought forth by Section 6 is discussed in the overall comments of this review and has been addressed by the authors.

Line 702: Nitric acid is most reactive with other radical species or reducing agents. It is not terribly reactive in the indoor environment – not close at all to the reactivity of OH. The small deposition velocity for NO comes from its slow reactivity with surface-bound materials. If there is more information about the reactivity of NO indoors, please cite.

Interactive comment on Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2020-300, 2020.