

Interactive comment on “Influence of aerosol copper on HO₂ uptake: A novel parameterized equation” by Huan Song et al.

Anonymous Referee #2

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The manuscript of Song et al deals with an important theme in atmospheric science; the interaction of HO₂ with particles containing dissolved copper and the modelling of the impact of this heterogeneous reaction on e.g. O₃ production.

Song et al have analysed laboratory data and derived an empirical expression that they then implemented in a model. They suggest that their parameterisation is superior to taking a constant value of 0.2 for the uptake coefficient. This is most likely true but why do they not compare to other parameterisations of this process, e.g. that proposed by IUPAC which also considers laboratory studies up to 2016 and which has a physical basis (i.e. aqueous phase rate coefficients for reaction of HO₂ / O₂⁻ with Cu).

They also do not consider in any detail the potential for organic content of particles to reduce the uptake coefficient considerably as this is mentioned only in passing on

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line 312-315. This aspect will be central to improving the modelling of HO₂ uptake to particle matter, as has been shown e.g. for N₂O₅. The sentence on line 149-150 in this regard is highly misleading: “Without the interference of organic matter, it is convenient to explore the mechanism of HO₂ heterogeneous uptake and derive its parameterized equation, which provides a good reference for the heterogeneous uptake of HO₂ in the actual atmosphere environment”. The co-authors from Jülich will be intimately familiar with this aspect of heterogeneous chemistry and should be able to provide input.

The manuscript is illogically organised and difficult to follow, has different definitions of the same term, poor language quality and incorrectly cites the published datasets of Lakey et al (2016) (see author comment from D. Heard). This work might be publishable after major revision and reorganisation.

Some specific points are listed below:

L11 hydroxyl peroxy radicals = hydroperoxyl radicals L12 gamma_HO₂ is defined but the expression after line 17 simply lists gamma. L15 parameterisation of HO₂? Presumably of HO₂ uptake

Does it make sense to list the expression in the abstract, where none of the terms (e.g. ALWC, [PM], Rd) involved are defined

L39-40 Meaning obscure. I think the authors refer to the reduction of aerosol mass over the last few years. The information that the uptake coefficient used (in calculating surface ozone) was 0.2 is superfluous here.

L57 L is defined as the aerosol liquid water content. In the abstract it is ALWC.

L68 MARKM model is otherwise referred to as MARK

L74 Equilibrium constant have capital “K”. Rate coefficients have lower case “k”.

L/3 H₀ is estimated (Thornton et al, 2008) to be 3900 M atm⁻¹. Why is this cited in different units to the effective solubility (H^{cc}). How good is this “estimate” and on what

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data is it based (I believe Hanson 1992, who also lists a T-dependence) ?

L101 Define $[xi]_{\text{equ}}$. In the line above only $[xi]$ is mentioned.

L105 “steady-state” HO₂ concentration. Why “steady-state” ?

L110 k_{eff} is listed in the equation 11. This appears to be defined 57 lines later, but not always in the same manner.

Tab1 (and abstract) the accommodation coefficient is not defined, as far as I can see.

Tab1 The data of Lakey 2015/2016 and Zou 2019 are not mentioned (Moon = Lakey ???)

Tab2 Add units, do not capitalize K and move to supplementary information Tab3 K should be capitalized (eqm.)

L146 annual average contribution. Does this refer to a global average ?

Fig1 Please explain why the uptake coefficient continues to increase at pH > 5 whereas k_{eff} decreases.

L166 k_{eff} is defined as a comprehensive reaction rate constant. . . . during heterogeneous uptake. On L210, K_{eff} is defined as the rate of HO₂ aqueous reaction with copper ions.

L175 The parameterisations listed do not include that of IUPAC, which includes more recent laboratory data than those listed.

L180 Based on the data of Lakey et al, IUPAC list a rate coefficient for HO₂ (O₂⁻) with Cu ions of 5×10^5 . This is orders of magnitude lower than those listed.

Fig2 Why are the data of Lakey not listed (or are these Moon ??)

Fig2 Taketani also have uptake coefficients in the absence of Cu that are just as high as the single point at about 0.5 M. Why are the other datapoints of Taketani selectively omitted here?

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L188 what is the “current parameterised equation”. From whom is it?

L201 This text ignores the fact that the IUPAC parameterisation accurately reproduces the lab studies from Lakey et al. Is the empirical parameterisation that Song et al propose really superior to the IUPAC one, which has a physical basis?

L213 where does this expression for the uptake coefficient come from?

L265 section 3.4.2. could be move to SI

L312 The work of Lakey et al is cited. Where are their data? How much “lower” can the uptake coefficient be in the presence of organics?

L351 move section 3.4.5 to SI

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