

Answer to Short Comment 1 (Rolf Sander)

The authors would like to thank Prof. Rolf Sander for the careful reading of our manuscript and his valuable comments that will help us to clarify some points of our manuscript and correct a mistake.

Comment 1:

On page 13, you write: "Iron is completely part of the liquid or solid phase, so the Henry's law constant is estimated to more than $10^6 \text{ mol m}^{-3} \text{ Pa}^{-1}$ (Sander, 2015)", citing my compilation of Henry's law constants. However, iron is not included in my publication. I am now curious about the origin of the value $10^6 \text{ mol m}^{-3} \text{ Pa}^{-1}$.

Answer 1:

It was our mistake to insert the iron compounds into Table 1 (line 381). Sorry for that. At tropospheric conditions and in its different possible states in ISA the iron content stays completely within the condensed phase (either as liquid or as solid). Thus any discussion about its Henry constant is obsolete: at tropospheric conditions the Henry constant of iron is of infinite height. Table 1 is changed accordingly (no more mention of iron compounds).

Comment 2:

Transfer between the gas phase and the aqueous phase is not determined by short-lived radicals like $^{\circ}\text{Cl}$ and $^{\circ}\text{OH}$, as you indicate in Fig. 3. Instead, longer lived molecules like H_2O_2 , Cl_2 , and HOCl determine the distribution between the phases. Thus, it is not sufficient to consider only the Henry's law constants of OH and Cl .

Answer 2:

We agree that the short living radicals $^{\circ}\text{Cl}$ and $^{\circ}\text{OH}$ recombine very fast to Cl_2 , H_2O_2 , and HOCl .

Iron exists at least in part as Fe(III) during nighttime and at least in part as Fe(II) during daytime. The methane oxidation by $^{\circ}\text{Cl}$ and $^{\circ}\text{OH}$ is restricted to the daytime because during night hours $^{\circ}\text{Cl}$ and $^{\circ}\text{OH}$ recombine fast to Cl_2 , HOCl , and H_2O_2 in the dark (**von Glasow, 2000**). During daylight hours these recombination products photolyze again by regeneration of the radicals. But even during day time these radicals and their recombination products co-exist because the cycling between $^{\circ}\text{Cl}$, $^{\circ}\text{OH}$, Cl_2 , HOCl , and H_2O_2 . This cycling is activated by sunlight photolysis and radical recombination reactions (**von Glasow, 2000, Luna et al. 2006**).

As we learn from Henry's law constants in Table 1 the oxygen species $^{\circ}\text{OH}$ and H_2O_2 have a much higher tendency to stay in the liquid phase than the chlorine species $^{\circ}\text{Cl}$ and Cl_2 . Cl_2 has the tendency to react with water of neutral pH by producing HOCl . But the pH values of ISA, especially if ISA is emitted as acid flue gas plumes are lower than 3. Within this acidic region the tendency of HOCl generation from Cl_2 decreases to very low values and even at those humidity levels when the ISA particles become deliquescent the majority of the activated chlorine species will be localized in the CH_4 containing gaseous phase, not in the liquid phase.

But even $^{\circ}\text{OH}$ may leave the condensed phase into the gaseous phase at favorable circumstances into the gaseous phase (Nie et al., 2014) and may contribute there to the oxidation of CH_4 during clear dry conditions without liquid phase at the Fe(III) surfaces.

These informations are inserted on a new column of Table 1 as follows:

Table 1: the Henry's law constants (Sander 2015) and daylight stability for different gaseous or vaporous components reacting with or produced by ISA in the troposphere

Substance	Henry's law constant [mol m ⁻³ Pa ⁻¹]	Stability against tropospheric day light (+ stable; - unstable)
CH ₄	1.4 x 10 ⁻⁵	+
°Cl	2.3 x 10 ⁻²	+
Cl ₂	9.2 x 10 ⁻⁴	-
HCl	1.5 x 10 ¹	+
HOCl	6.5	-
°OH	3.8 x 10 ⁻¹	+
H ₂ O ₂	8.3 x 10 ²	-

Bibliography:

Luna, A. J., Nascimento, C. A. O., and Chiavone-Filho, O. (2006). Photodecomposition of hydrogen peroxide in highly saline aqueous medium. *Brazilian Journal of Chemical Engineering*, 23(3), 341-349.

von Glasow, R.: Modeling the gas and aqueous phase chemistry of the marine boundary layer. Ph.D. thesis, Univ. Mainz, Mainz, Germany, 2000 (Available at www.rolandvonglasow.de).