

# ***Interactive comment on “Climate engineering by mimicking the natural dust climate control: the Iron Salt Aerosols method” by Franz Dietrich Oeste et al.***

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We would like thank Prof. Cornelius Zetzsch for reading our manuscript and for his valuable comments about section 5.

The entire comment of Prof. Zetzsch concentrates to the discussion in chapter 5.2 of the manuscript about the estimation of Wittmer et al., 2015a to the amount of ISA iron required for a significant CH<sub>4</sub> depletion increase by atomic Cl generation.

Overall comment: The comments from Prof. Zetzsch are concluded at the end of page C5 by: “The technical application of ISA for climate engineering (how to obtain and apply a finer size distribution of FeCl<sub>3</sub>, FeOOH or Fe<sub>2</sub>O<sub>3</sub> or coatings of sublimed

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FeCl<sub>3</sub> on solid carrier particles or to add iron-containing compounds to the fuel of combustion engines and power plants) is beyond the scope of our studies. The global comment (all the other pages) states that the experimental results described by Wittmer et al. (2015a, 2015b and 2016) are the first quantitative determination of the source strength of iron(III) photolysis-induced atomic Cl from aerosol and that the results are an experimental basis of the ISA method and that the conservative estimation of Wittmer et al., 2015a should not be involved into extrapolations to the real atmosphere and for climate engineering.

Reply: In the Wittmer et al., 2015a article the following sentences were found: “Furthermore, iron-doped sea-salt aerosols have been proposed as a method for climate engineering, aiming to enhance CH<sub>4</sub> depletion with higher Cl levels in the marine boundary layer and to simultaneously fertilize the oceans<sup>95</sup>). Based on our results, one may try to estimate the feasibility of such a project<sup>95</sup>”. The concluding comment and statement of Prof. Zetzsch seems to contradict these sentences. These sentences and ref. 95 from the Wittmer et al., 2015a article refer to the ISA method variants 2 and 3 (chapter 6 of our manuscript) described by Meyer-Oeste, 2010 and this reference is the proof that the cited statement aims directly to the ISA method and “The technical application of ISA for climate engineering”. Furthermore, part of this work of Wittmer et al. has been presented in 2014 at the first “Climate Engineering Conference” in Berlin (Wittmer et al, 2014).

Comments of pages C4 and C5. These comments relate to page 40 lines 1246-1275 of the manuscript.

Reply: We took into account Prof. Zetzsch comments, we suppressed the word “wrong” and replaced the paragraphs concerned by the following sentences in the manuscript:

“Current CH<sub>4</sub> depletion by °Cl is estimated from 3.3% (Platt et al., 2004) to 4.3% (Allan et al., 2007). According to the results of Wittmer (Wittmer et al., 2015b) at a Cl-/Fe(III) molar ratio of 101, this amount would rise fourfold: from 13 to 17%. 1. Wittmer et al.

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used their results obtained at a Cl-/Fe(III) ratio of 51 at the pH of 3.3-3.5:  $1.9 \times 10^5$  °Cl/cm<sup>3</sup>. We consider that this pH is suboptimal. Instead it should be used the results obtained at a Cl-/Fe(III) ratio of 101 at the pH of 2.1-2.3:  $1.9 \times 10^5$  °Cl/cm<sup>3</sup>. Moreover, Wittmer et al. made two limitative estimations: 2. They only focused on the Cl delivery in the condensed state by coagulation as Cl- transfer option between ISA particles and the Cl source sea-salt aerosol ignoring other Cl sources, Cl aggregate states, and Cl transfer mechanisms. According to this model the ISA particles should lose in the daylight continuously their Cl- load by °Cl emission and as a consequence they could gain back Cl only by coagulation with sea-salt aerosol particles. As further consequences of this model the Cl-/Fe(III) ratio of ISA particles would decrease, their diameter increase and their residence time in the troposphere would decrease. But according to Graedel and Keene (1996) and Keene et al. (1999) the next prominent source of inorganic Cl in the troposphere beside sea-salt aerosol is vaporous HCl. This is the main source the ISA particles can refill the chloride lost by photolysis. The main Cl uptake mechanism from this Cl source is the sorption from the gaseous phase. Main HCl sources are the sea-salt reaction with acids, CH<sub>4</sub> and further hydrocarbon reactions with °Cl (Keene et al., 1999), flue gases of coal, biomass and garbage combustion (McCulloch et al. 1999), as shown in the global Reactive Chlorine Emissions Inventory (Keene et al., 1999), HCl from chlorocarbons being a significant part (Sanhueza, 2001) in particular from CH<sub>3</sub>Cl which is the largest, natural contributor to organic chlorine in the atmosphere (Lobert et al, 1999). 3. They estimate that the global production rate of 1785 Tg/year of sea-salt aerosol Cl- has to be doped with iron at a Cl-/Fe(III) molar ratio of 51 meanwhile we consider it has to be estimated at a molar ratio of 101 (according to 1.). The calculations made with these limitative assumptions resulted in an iron demand of 56 Tg/year Fe(III) to obtain the desired CH<sub>4</sub> depletion effect (Wittmer et al. 2015a). Whereas the calculations with a Cl-/Fe(III) ratio of 101 results in a Fe(III) demand of only 18 Tg/year – still with the limitative assumption that there is no further Cl- source than sea-salt. ISA is produced from pyrogenic iron oxides. Pyrogenic oxides have particle sizes lower than  $0.1 \mu\text{m}$ . Diameters of the NaCl-diluted ISA particles of

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the Wittmer tests (Wittmer et al. 2015a) are round about  $0.5\mu\text{m}$ . This confirms the test results of Wittmer et al. as calculation basis without any cut. But Wittmer et al. made two other limitative assumptions: 4. ISA has the same particle size and corresponding surface range as sea-salt; 5. ISA has the same residence time as sea-salt aerosol in the troposphere.”

Comment page C5 (beginning): “Pyrogenic oxide particles smaller than  $0.1\mu\text{m}$ , as proposed by the authors, are not covered by our estimation. The pH of the aerosol droplets (p. 39, lines 1233 and 1234) was not measured, but the pH of the stock solution (1 g NaCl per liter, doped with  $\text{FeCl}_3$ ), that is atomized to obtain the optimum size of the aerosol droplets. The pH of the droplets was not measured in our work. The low pH is a consequence of hydrolysis of  $\text{FeCl}_3$ , and the gas phase is expected to contain the HCl gas volatilized from the atomized droplets of the stock solution. Åž

Reply: We agree that these particle sizes are not covered by Wittmer et al. estimations. As a matter of fact, known salt aerosol generation methods by vapor condensation or nebulization (Gupta et al., 2015; Biskos, et al. 2006) allow not only the flame descending ISA type 1 (Oeste, 2004), but also the condensation and nebulization descending ISA variants 2 and 3 to be produced with aerosol particle diameters between  $0.1$  and  $0.01\mu\text{m}$ . Diameters of salt aerosol particles according to these physical aerosol generation methods are up to, or more, than one order of magnitude smaller than of those used in the experiments by Wittmer et al., 2015a. According to Lim et al., 2006 and to Meyer-Oeste, 2010 the optimum  $^\circ\text{Cl}$  production by sunlight photolysis of  $\text{FeCl}_3$  solutions or ISA is generated in the acidic pH range. The efficient  $^\circ\text{Cl}$  generation is necessary for an efficient  $\text{CH}_4$  depletion ISA. Except if made by condensation and hydrolysis of  $\text{FeCl}_3$  vapor or by nebulization of pure  $\text{FeCl}_3$  solution, or produced by combustion to pyrogenic  $\text{FeOOH}$  and reaction and hydrolysis with HCl and  $\text{H}_2\text{O}$  to  $\text{FeCl}_3$  solution:  $\text{FeCl}_3$  has an acidic pH from the beginning because it hydrolyses according to equation 1.

equation 1:  $\text{FeCl}_3 + 2\text{H}_2\text{O} \rightarrow \text{FeCl}_2\text{OH} + \text{H}_3\text{O}^+ + \text{Cl}^-$

Wittmer et al., 2015a referred to the ISA method (Meyer-Oeste, 2010) but in their extrapolation, they did not take into consideration the required pH of the ISA method.

Comments from page C5: We did not claim that the optimum efficiency of Cl production occurs at pH 2 and independent of the distribution of HCl between gas and particle: the lower the pH the less chloride will be available in the particle phase. For HCl adsorbed on humidified Fe<sub>2</sub>O<sub>3</sub> (Wittmer and Zetzsch, 2016), the optimum pH will be much lower than 2 since this may dissolve some of the iron(III). Finally, we would not like to further discuss our simplifying assumptions 2. to 5. (p. 40, line 1246-1275). These were meant to be restricted to Fe doped NaCl aerosol alone, implying an uncertainty of more than an order of magnitude of our estimate. We agree with the argument 6. (line 1276-1282) that the larger specific surface of combustion-derived Fe<sub>2</sub>O<sub>3</sub> is promising. This is the reason why we had started to look into the interaction of a pyrogenic Fe<sub>2</sub>O<sub>3</sub> material (characterized by Mössbauer spectroscopy) with HCl gas (p 43, line 1383).

Reply: According to our chapter 2.2 the coagulation of small particles within aerosol plumes is retarded. Otherwise known bridging of intercontinental distances and particle abundance in polar glacial regions of these particles would be impossible. Wittmer et al., 2015a considered only sea-salt aerosol particles as transport vehicles for ISA and as only possible contact medium to gain chloride ions as <sup>o</sup>Cl source. It is well known that coal combustion is a major source of active chlorine (McCulloch et al., 1999; Keene et al., 1999; Sanhueza, 2001) as well as iron (Sedwick et al., 2007; Luo et al., 2008; Wang et al, 2015; Ito et al, 2016), thus both iron and chlorine are jointly issued by other mechanisms and sources. As stated in our chapter 5.2 below point 5, sea salt aerosol has residence times in the troposphere lower than one day according to its coarse particle diameters without any possible bridging of intercontinental distances. In reality the chloride transfer between sea-salt aerosol particles and ISA particles may take place without any touch or coagulation because the troposphere is an acidic environment. Troposphere is a source of organic and inorganic acids which are in permanent con-

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tact with the sea-salt aerosol. The acid ingredients in contact with sea spray produce HCl. Further ISA is produced by combustion and even becomes elevated by flue gas plumes: acid precursors like SO<sub>2</sub> or NO<sub>x</sub> are in higher concentrations within the flue gas plume comparing to the tropospheric environment. The acids generated by flue gas plume produce additional HCl by reaction with the sea-salt aerosol (von Glasow, 2000). As a result, ISA and ISA precursors may absorb any chloride requirement via HCl vapour from the sea-spray source by itself (Wittmer et al. 2016).

As a conclusion: Prof. Zetzsch comment did not present arguments against the results of our own extrapolations. We agree that extrapolations about the ISA requirement should be supported in the future by detailed model calculations, but the generation of such models and future experimental work will be the subject of separate articles.

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