

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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In section 5, this manuscript discusses our estimate for the amount of dissolved Fe(III) in sea-salt aerosol required for a significant global increase of atomic Cl. Our experiments obtained the first quantitative determinations of the source strength of atomic Cl from iron doped salt pans (Wittmer et al., 2015a) and aerosol droplets (Wittmer et al., 2015b) as an experimental basis of the ISA method, and we wanted to give a conservative estimate on the basis of our salt-aerosol experiments and not to be involved into extrapolations to the real atmosphere (which would require detailed global model calculations).

In contrast to a salt pan, the aerosol technique has the advantage that we can calculate

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the surface area of the aerosol from the measured size distribution and number density. This calculation required a minor correction for deposited aerosol on the chamber wall, where it was found to be less efficient in the production of atomic Cl. The correction procedure was described in Wittmer et al., 2015b, as follows:

“To quantify the particle deposition and its contribution to the active surface area (and thus to Cl activation), a test measurement was performed to determine the fraction of Cl release by the active wall surface compared with the active aerosol surface: the iron-doped artificial seawater sample (Cl /Fe(III) = 13) was injected and allowed to deposit totally for 17 h (<0.005 % of the surface area should have remained suspended) while keeping the RH at 80 %. Then the ‘aerosol-free’ chamber was irradiated, resulting in a Cl production that was 20 ± 4 % compared with the actual production measured for the same sample in an aerosol experiment (see section 3.3.2: Iron(III)-catalysed Cl atom production). This production was evaluated by taking the mean of the quotient of each total production (deposited and not deposited) normalised by the respective initial LWC directly after injection. In Eqn 3.3, the contribution of deposited, active aerosol surface area is accounted for by adding 20 % of the deposited surface area since the time of injection to the surface area when the lights were turned on (corrected for deposition).” Contour plots of the time-dependent size distributions are displayed in the supplementary material of our work.

The simulated salt pan has the disadvantage that the size and the surface of the crystalline grains are hard to characterize and that the depth of the quasi-liquid layer involved in the exchange with the gas phase is not well-defined because of its dependence on relative humidity. Control of relative humidity would require temperature control of the salt layer that is irradiated by a strong, bifocal solar simulator. The aerosol chamber has the advantage that the size distribution of the droplets can be characterized and that the required close contact between gas and liquid is established in a well-mixed and thus fairly homogeneously irradiated volume of air. The Köhler equation then describes the hygroscopic, deliquescent behavior of the FeCl₃ doped salt

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droplets.

We estimated the efficiency for Cl generation (p. 39, line 1226) from observed concentrations of atomic Cl (atoms per cm³) in simulation chamber experiments and calculated the corresponding source strengths (atoms per cm³ per hour) from the quasi-stationary state, established between the photochemical production of Cl and its consumption by reaction with the test mixture of hydrocarbons present in the gas phase (in the absence of any other reactants for the atomic Cl – the zero air contained less than 1 ppb of O₃, less than 0.5 ppb of NO_x and about 100 ppb of CH₄). The observed concentrations are high because the aerosol surface in our chamber (10000-30000 μm² per cm³) is about 150 times higher than in the marine boundary layer, where it is ~60-200 μm² per cm³ according to Warneck (1999). One may calculate the source strength per square cm of aerosol surface and try to base the calculation on this information, assuming a linear relationship. The inherent loss of aerosol surface by deposition was monitored in our experiments and considered in the calculation of the source strength that was corrected for a minor catalytic influence of the deposits on the chamber walls.

In our conservative estimate, we simply refer to the amount of dissolved Fe(III) in sea-salt aerosol corresponding to the performed experiments. According to Keene et al. (1990), 1785 Tg Cl- dissolved in sea salt are produced annually. To obtain a molar Cl-/Fe(III) ratio of 51, a mass of 56 Tg dissolved Fe(III) would be necessary according to the molar masses. Comparing the blank experiment (artificial sea salt without Fe(III), producing $0.3-0.4 \times 10^{21}$ atoms cm⁻² h⁻¹) to the Cl-/Fe(III) = 51 experiment (producing $1.4-1.5 \times 10^{21}$ atoms cm⁻² h⁻¹ with a fairly constant rate), one can estimate a fourfold increased production of Cl radicals in the gas phase. Based on the 150-167 times higher available aerosol surface area in our chamber, the fourfold increase was scaled down to 0.024-0.0267 (4/150 and 4/167) which corresponds to ≈2.5 %. The same, simple calculation was performed to estimate the 17-19 % increase when aiming for Cl-/Fe(III) = 13.

Going along the criticisms raised by Oeste et al., we justify our assumptions with the

following comments:

1. Instead of using a Cl-/Fe(III) molar ratio of 101, Wittmer used a Cl-/Fe(III) ratio of 51 to perform calculations at the suboptimal pH of 3.3-3.5: 1.9×10^5 Cl/cm³ (Wittmer et al., 2015a);

Comment: We used a ratio of 51 since we hardly saw a significant effect with a ratio of 101 (see figure 3.4 in Wittmer et al., 20156). However, the low pH experiment (pH 2.1-2.3) is an error-prone basis for an estimate, since the pH is far away from the pH of the blank experiment (4.7-5.0). A blank experiment at such a low pH would be more suitable for a better estimation where also a higher Cl production can be expected. We admit that in our work we had a pH of 3.3-3.6 (see Table 3.2 in Wittmer et al, 2015b), and thus the fourfold increase is probably overestimated since a higher Cl production in the blank – due to a lower pH – would lead to a lower relative increase when adding Fe(III).

2. There is no other tropospheric Cl- source than sea-salt; Comment: This claim is correct for the conditions of our chamber, where other sources are considered by the blank experiment. We just assumed sea-salt as a Cl source since we considered this source in our experiments alone (induced by already dissolved Fe(III) in a sea-salt matrix).

3. The global production rate of sea-salt aerosol Cl- of 1785 Tg/year has to be doped with iron at a Cl-/Fe(III) molar ratio of 51. Comment: See comment on criticism 1.

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 to 4. and 5.: We do not claim that our estimation counts for the ISA particles. As described in our text, the estimation is focused on the Cl production by sea-salt aerosol (ignoring other sources). We only refer to the required amount of dissolved Fe(III) in the sea-salt aerosol compared to our experiments. Pyrogenic oxide particles

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smaller than 0.1 μm , 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 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 FeCl_3 , and the gas phase is expected to contain the HCl gas volatilized from the atomized droplets of the stock solution. The lifetime reduction of CH_4 in the troposphere (p. 36, line 1236) does not correspond to the lifetime reduction in the aerosol chamber but would depend on the vertical distribution of the ISA in the troposphere in comparison with the vertical distribution of CH_4 . 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_2O_3 (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_2O_3 is promising. This is the reason why we had started to look into the interaction of a pyrogenic Fe_2O_3 material (characterized by Mössbauer spectroscopy) with HCl gas (p 43, line 1383). The technical application of ISA for climate engineering (how to obtain and apply a finer size distribution of FeCl_3 , FeOOH or Fe_2O_3 or coatings of sublimed FeCl_3 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.

Bibliography:

Keene, W. C., Khalil, M., Aslam K., Erickson, D. J., McCulloch, A., Graedel, T. E.,

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Lobert, J.M., Aucott, M. L., Gong, S. L., Harper, D. B., Kleiman, G., Midgley, P., Moore, R. M., Seuzaret, C., Sturges, W. T., Benkovitz, C. M., Koropalov, V., Barrie, L. A., Li, Y. F., 1999. Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive chlorine emissions inventory. *J. Geophys. Res.* 104, 8429-8440.

Warneck, P., 1999. *Chemistry of the Natural Atmosphere*, Academic Press, San Diego.

Wittmer, J., Bleicher, S., Ofner, J., Zetzsch, C., 2015a. Iron (III)-induced activation of chloride from artificial sea-salt aerosol. *Environmental Chemistry* 12, 461-475.

Wittmer, J., Bleicher, S., Zetzsch, C., 2015b. Iron (III)-induced activation of chloride and bromide from modeled salt pans. *J. Phys. Chem. A* 119, 4373–4385.

Wittmer, J., Zetzsch, C., 2016. Photochemical activation of chlorine by iron-oxide aerosol. *J. Atmos. Chem.* DOI 10.1007/s10874-016-9336-6

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