INTERNSHIP REPORT

ON

METHANE REMOVAL BY IRON SALT AEROSOLS

By

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Outline and objective

Atmospheric methane contributes significantly to global warming despite its short chemical lifetime of around one decade. Methane is removed from the atmosphere naturally by oxidation via OH radicals and, to a lesser extent, Cl radicals. The initial oxidation by Cl radicals is 16 times faster than oxidation by OH, however the Cl pathway removes 50 times less CH_4 due to a much lower concentration of atmospheric Cl radicals.

It has been suggested that releasing Cl into the atmosphere could enhance the rate of methane oxidation[1–3] and hence reduce its contribution to global warming. However, there are significant uncertainties in both the mechanism of release and in the effectiveness of injecting Cl or Cl precursors into the atmosphere.

One suggested method of generating atmospheric Cl radicals is enhancing a natural mechanism by which Cl is released. The Mineral Dust Sea-spray Aerosol (MDSA) mechanism occurs when iron-rich dust from the Sahara is blown over the ocean: as it mixes with sea-spray, aqueous iron chloride species form, which can undergo photolysis and hence release Cl_2 gas through a series of non-linear cycles[1,4]. Liberation of Cl from sea-spray via this mechanism has shown to be catalytic in Fe, and it has been suggested that it could also be catalytic in Cl if HCl (one of the products of CH_4 oxidation by Cl) is taken up into the aerosol[5]. This Cl source could be anthropogenically mimicked by releasing Cl-containing iron aerosol into the atmosphere (iron-salt aerosol, ISA).

In this project I aim to simulate the release of Cl from these precursors using a kinetic box model, and to study the impacts that Cl release could have in the marine boundary layer. The focus is on uncertainty quantification and identifying the main areas of uncertainty in the kinetics of the process. T

Methodology

The model was implemented in BOXMOX[6]. The initial model used equations from Pennacchio et al.[7] and was implemented in a similar manner to the way described in the original paper. I initially ran simulations releasing Cl radicals at different rates into the box model and monitoring the time evolution of CH_4 during and after the release. As per Li et al.[2] my Cl emissions were spaced between 10 and 2000 Tg yr^{-1} of molecular Cl. A script for rate of production analysis was also developed to allow inspection of the reaction fluxes for a given species at a given time.

To implement the aqueous phase chemistry for Fe-catalysed Cl release from ISA, I used the iron-aerosol cycles shown in Oeste et al.[8] and Mikkelsen et al.[5] combined with equations and rates reported by Wittmer et al,[9–11] and Lim et al.[12]. The cycles between $[Fe(OH_2)_6]^{2+}$, $[Fe(OH_2)_6]^{3+}$, $[Fe(OH_2)_5(OH)]^{2+}$, and $[Fe(OH_2)_5Cl]^{2+}$ is show in

Figure 1. The Cl and OH cycles, shown in Figures 2 and 3 respectively, interlock with the Fe cycles shown in Figure 1 to give a series of non-linear radical chains.

After initial runs of this model, it was noted that neither the HCl dissociation to form anionic Cl nor the speciation of $[Fe(OH_2)_6]^{3+}$ to $[Fe(OH_2)_5OH]^{2+}$ and $[Fe(OH_2)_5Cl]^{2+}$ had been implemented. Successful implementation of these was limited by the time available for the project.

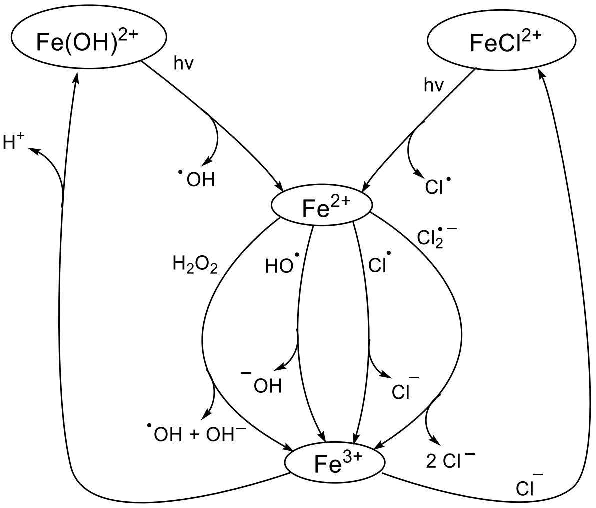


Figure 1: Aqueous phase cycles between Fe(II) and Fe(III) species in a low pH, Cl-containing environment with (OH_2) ligands excluded

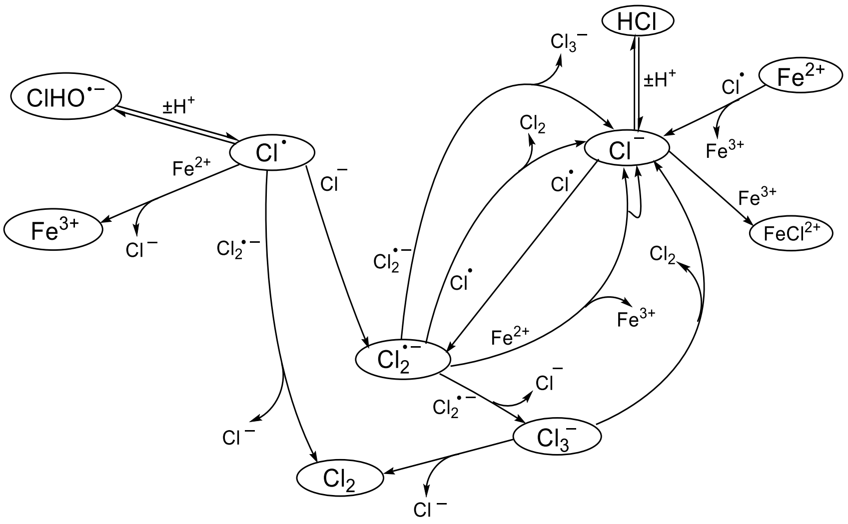


Figure 2: Aqueous phase Cl species cycles

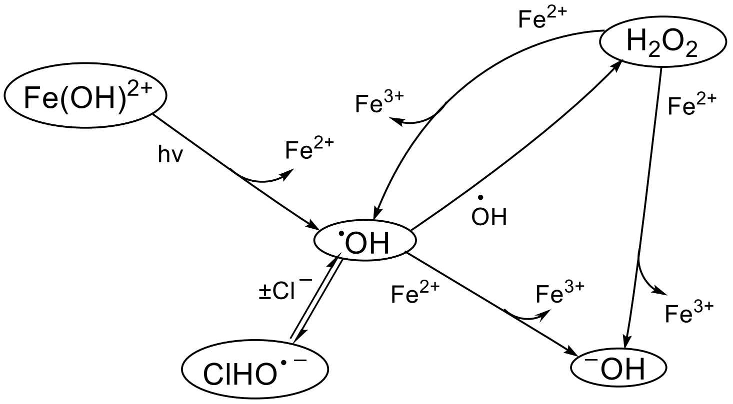


Figure 3: Aqueous phase OH species cycles

The steady state conditions of my initial model implementation, without ISA chemistry, had a CH_4 concentration of 2.16 ppm, and O_3 concentration of 30 ppb, and OH and NOx concentrations of $3.7*10^6$ and $4.9*10^8$ respectively.

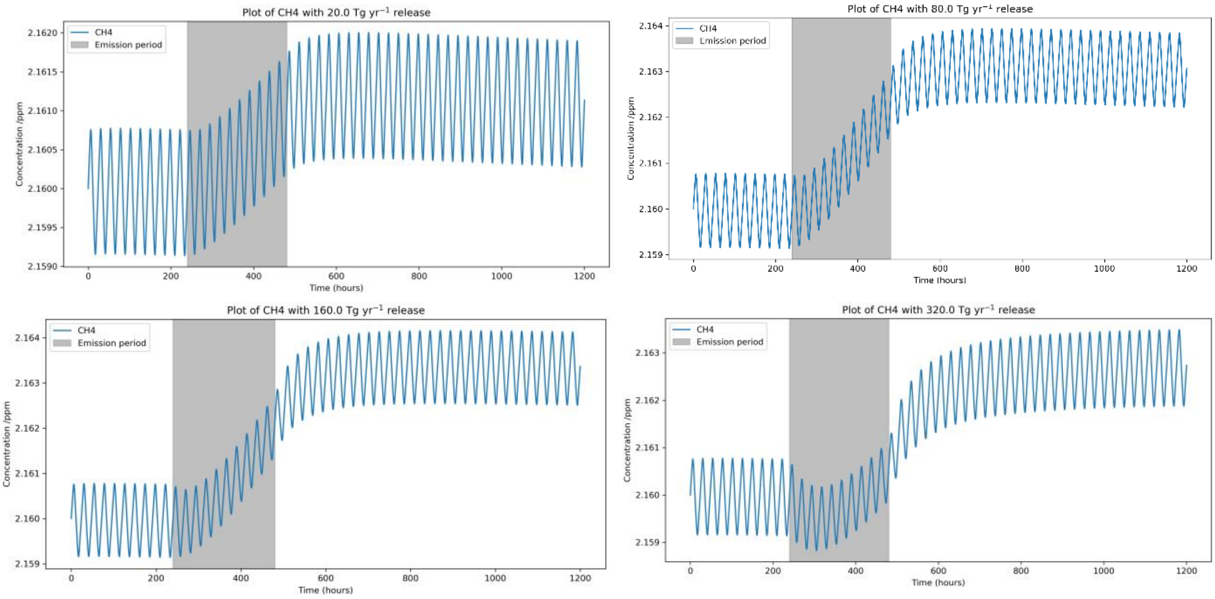
Initial model

Initial Cl release experiments of 20, 80, 160 and 320 Tg yr^{-1} Cl release for 10 days caused an overall increase in CH_4 concentration in the atmosphere, shown in Figure 4. This is likely due to suppression of OH production due to Cl radicals removing O_3, shown in reactions 1-3 below.

$$1.16 \times 10^{-11} \ : \mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O2} \ (1)$$

$$2.95 \times 10^{-5} \ : \mathrm{O_3} + \mathrm{h\nu} \rightarrow \mathrm{O_2} + \mathrm{O(^1D)} \ (2)$$

$$2.14 \times 10^{-10} : \mathrm{O(^1D)} + \mathrm{H_2O} \rightarrow \mathrm{OH} + \mathrm{OH} \ (3)$$


Plot of CH4 with 20.0 Tg yr^{-1} release

Plot of CH4 with 80.0 Tg yr^{-1} release

Plot of CH4 with 160.0 Tg yr^{-1} release

Plot of CH4 with 320.0 Tg yr^{-1} release

Figure 4: CH_4 concentration with 20, 80, 160, and 320 Tg yr^{-1} Cl release into the model for 10 days (top left to bottom right)

At releases greater than 380 Tg yr^{-1} it was found that CH_4 concentration had decreased overall by the end of the 10-day period but then subsequently increased again after the release period had stopped. I also tried 380 Tg yr^{-1} of Cl for a longer period, 20 days, however this release rate now caused an initial decrease in CH_4 concentration followed by an increase during the period of emissions (Figure 5).

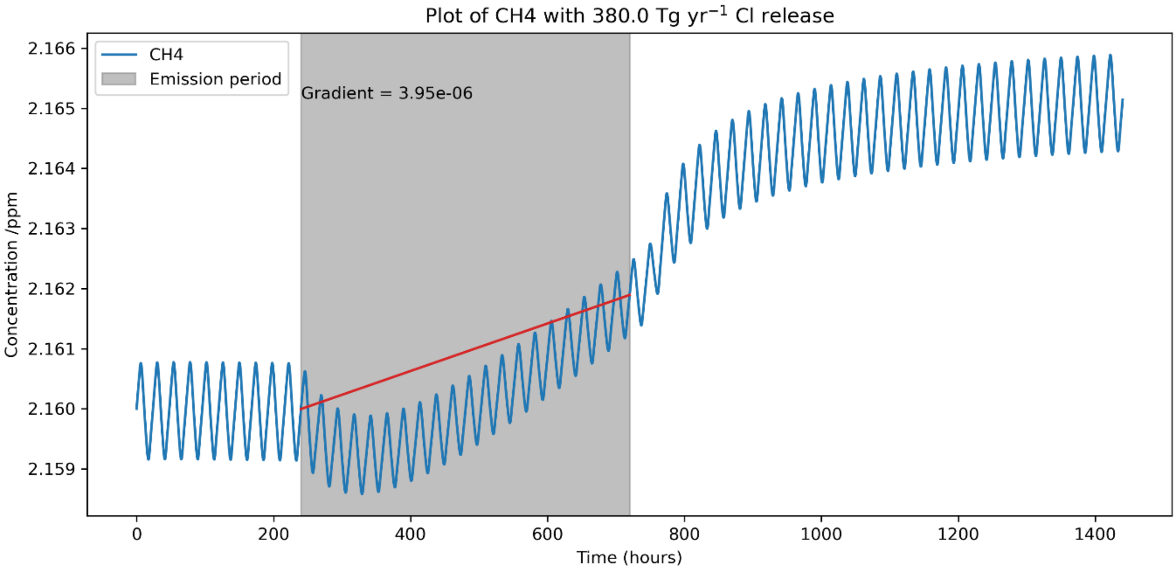


Figure 5: CH_4 concentration with a 20 day release of 380 Tg yr^{-1} Cl

This increase continued even if the emissions were maintained for a period of 10 years. The concentrations of atmospheric Cl and OH are shown in Figure 6.

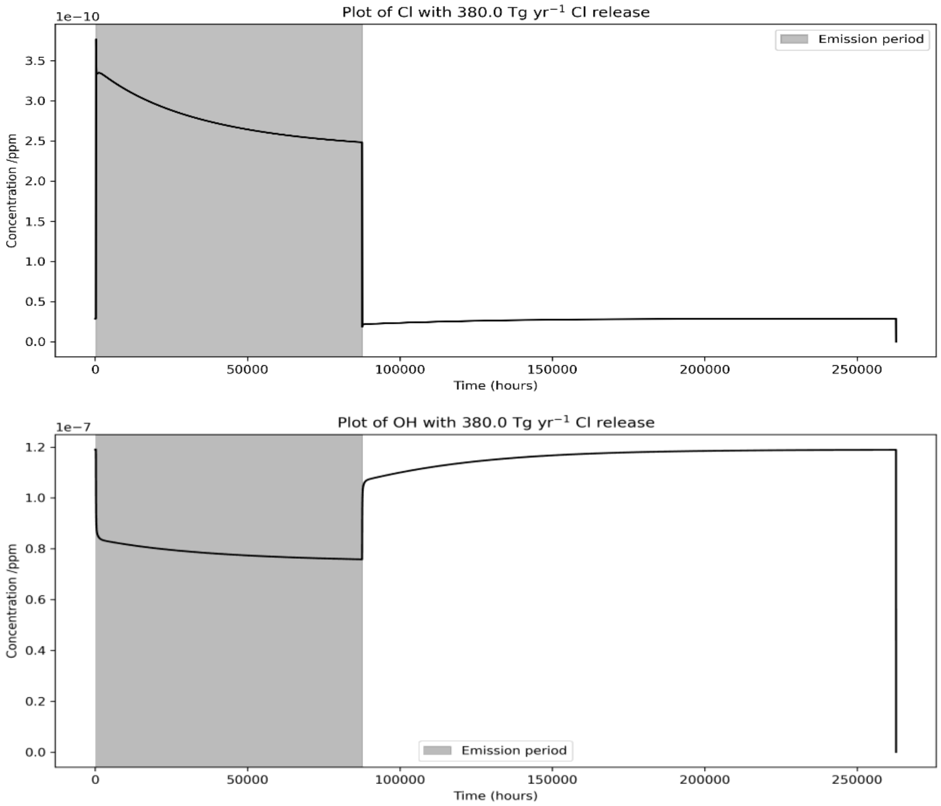


Figure 6: Alteration of Cl and OH concentrations due to atmospheric Cl release of 380 Tg yr^{-1} for 10 years

This response to long-term Cl release continued to be seen at 700 Tg yr^{-1} Cl, however at 1000 Tg yr^{-1} release it was seen that the concentration of CH_4 decreased significantly even during long periods of Cl release (Figure 7). This suggests that at this rate of Cl release, the suppression of the OH oxidation pathway is outweighed by the increased rate of the Cl oxidation pathway, and that this balance changes over a small range of Cl release rates. It is still seen that after release is stopped, the concentration of CH_4 begins to increase again.

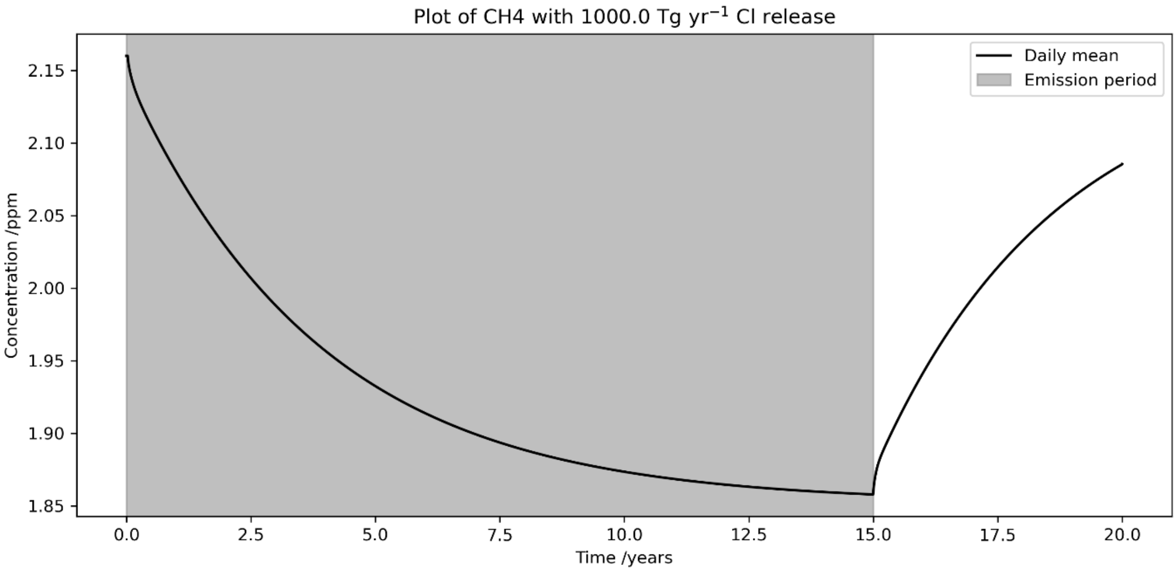


Figure 7: Decrease of CH_4 concentration in response to 1000 Tg yr^{-1} Cl release

Model runs where Cl is released during only the day or only the night had no significant benefit over constant Cl release. Moreover, double the rate of Cl release was needed to reduce CH_4 burden if Cl was released during only the day or night to counteract the shorter release time.

Model with ISA

The aqueous phase chemistry was then implemented into the model. With no emissions of ISA, the model still appeared to be in a steady state. A release of 300 Tg yr^{-1} of ISA into the model lead to an overall increase in CH_4 burden during the release period (Figure 8). During this release, the atmospheric Cl levels increased to $3*10^3$ molecules cm^{-3}, whereas for the overall CH_4 oxidation rate to be increased, it was found in the base model that Cl concentration needed to increase to $1.5*10^4$ molecules cm^{-3}. Therefore, in the next model simulation, 1500 Tg yr^{-1} of ISA was released into the model. A very similar CH_4 profile to that in Figure 8 was seen despite the much larger release of ISA: inspection of the atmospheric Cl concentration showed that Cl concentration had only increased to $1.1*10^4$ molecules cm^{-3}, suggesting a nonlinear relationship between ISA concentration and atmospheric Cl concentration. A run with an even greater ISA release, 2500 Tg yr^{-1}, was conducted but once again a similar CH_4 profile to Figure 8 was seen despite atmospheric Cl concentration increasing to $1.75*10^4$ molecules cm^{-3}, greater than that needed to increase the overall methane oxidation rate in the base model. This could be due to the OH oxidation pathway being suppressed further by the aerosol than with only Cl being released. However, investigation into this was not possible due to time constraints with the length of the project. Once the aforementioned HCl dissociation and Fe^{3+} speciation were implemented into the model, no more successful runs were able to be carried out due to numerical issues and project time constraints.

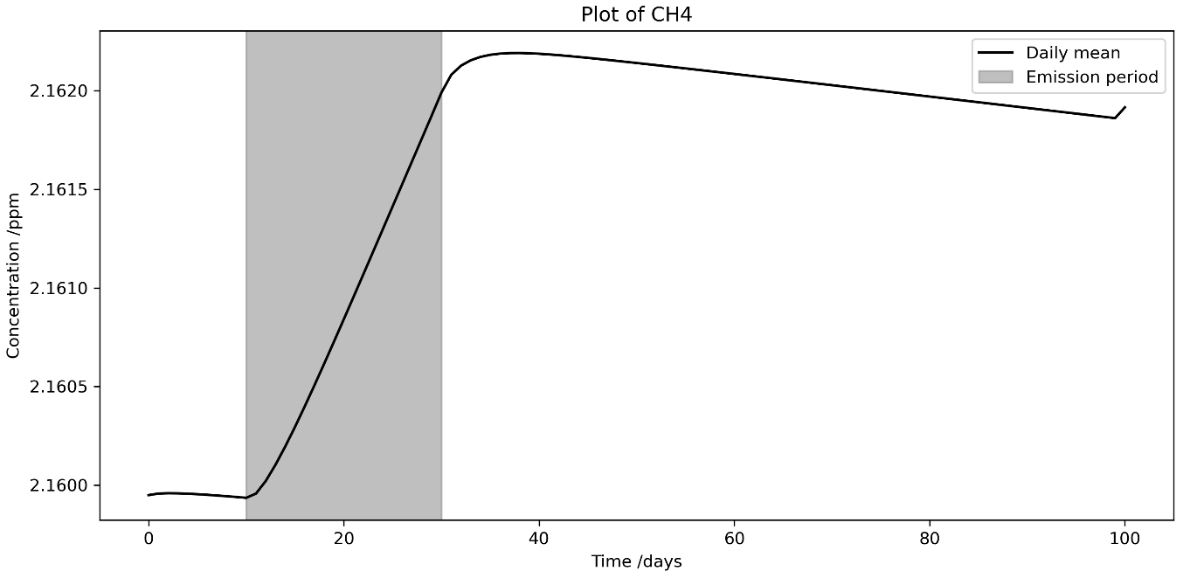


Figure 8: Plot of CH_4 concentration in response to 300Tg yr^{-1} ISA release

Uncertainties, limitations, and recommendations

The model was set up according to Pennacchio et al.[7] who excluded VOCs from the model, and compensated for this by constraining O_3 and NOx with fixed O_3 and NO_2 emissions and O_3 deposition. This introduced uncertainty into my model through uncertainty about the rates of emission and deposition that would give realistic atmospheric mixing ratio. It is possible that using a more comprehensive model that includes VOCs could also give a more realistic simulation of the background atmospheric chemistry, however provided that species with a significant impact on methane (OH, Cl and their precursors such as O_3, NOx, HCl) are well constrained, this may not have a significant impact. Furthermore, the reaction rates used in the model were temperature independent, and the photolysis rates used by the original paper were calculated for a tropical region but this model acted as if emissions were on a global scale. The photolysis rates were also all modified by BOXMOX's built-in "SUN" parameter which represents an arbitrary diurnal cycle between 4:30am and 19:30pm with a profile shown in Figure 9 which is calculated based on Equation 4.

$$\mathrm{SUN} = \frac{1 + \cos(\pi * \mathrm{time})}{2} \qquad (4)$$

Where "time" is as a fraction of the time between sunrise and sunset

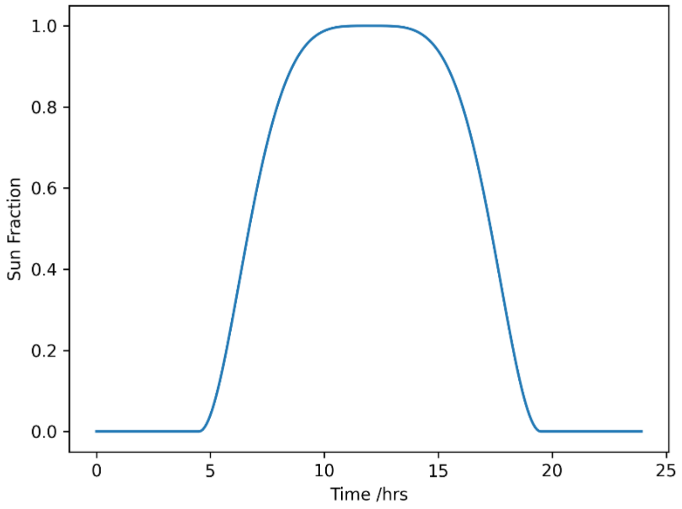


Figure 9: Profile of the BOXMOX “SUN” parameter over a 24-hour time period

Further investigation into the efficacy of releasing Cl into the atmosphere is required, as shown during the base model runs where an amount much larger than reported by Li et al.[2] was required before methane oxidation rate was increased. The reduction in OH production relative to the increase in CH_4 oxidation by the Cl pathway should be studied further to improve our understanding of the nonlinear relationship between Cl and CH_4 concentration.

During the first model runs with the updated ISA chemistry, where steady state conditions were tested, it was seen that there was a very small change in CH_4 concentration over a 5 year time period: a decrease of 0.004 ppm was seen when the model was run with a one hour time increment, but an increase of 0.00025 ppm was seen when the model was rerun with the same conditions but using a two hour time increment. This suggests that the model concentrations were more sensitive to the timestep parameter than initially thought, and more investigation should be done into whether the base model runs would give a different (increase vs. decrease) with a smaller timestep.

There is further uncertainty about the aqueous chemistry that was implemented to represent the ISA. The photolysis rates for the aqueous Fe (III) species were arbitrarily set to be faster than the oxidation of Fe(II) by H_2O_2 to allow Fe (II) to be the limiting rate, as described by van Herpen et al[4]. This was because, despite the quantum yields of $[Fe(OH_2)_5(OH)]^{2+}$ and $[Fe(OH_2)_5Cl]^{2+}$ being quoted by Lim et al.[12], cross sectional areas for these species could not be found. Furthermore, the oxidation rate of Fe (II) by H_2O_2 quoted by van Herpen et al.[4] is only for a given aerosol pH and H_2O_2 concentration, but was used (after unit conversion) as a constant rate for all pH and H_2O_2 concentrations.

There are also Fe species that were not included in the model such as $[Fe(OH_2)_4(OH)_2]^+$ and $[Fe(OH_2)_4Cl_2]^+$ due to their limited formation at low pH and slow rates of reaction. However, pH was not controlled in the model, and the exact implementation of the aqueous phase chemistry likely gave more significance to $[Fe(OH_2)_5(OH)]^{2+}$ and too little to $[Fe(OH_2)_4Cl_2]^+$ than it should have. Fe species in the aerosol were fixed to be in an initial ratio of $FeCl^{2+}$:Fe^{3+}:$FeCl_2^+$:$FeCl_3$ 50:25:20:5 before reaction however there was no mechanisms for $FeCl_2$+ and $FeCl_3$ to react within the model and no implementation of speciation after the initial ISA release.

When the model was run with ISA chemistry implemented, there was no mechanism by which Fe^{3+} reacted to form $[Fe(OH_2)_5(OH)]^{2+}$ and $[Fe(OH_2)_5Cl]^{2+}$ (Figure 1 does include these reactions), leading to Fe not being catalytic which is not representative of the MDSA mechanism. Similarly, there was no source of Cl^- anions in the aerosol, leading to a very low Cl^- concentration and hence slow rates of reaction within the Cl cycles (Figure 2). Both of these were changed by assigning rates to the Fe reactions and the dissociation of HCl dissolved in the aerosol based on their respective equilibrium constants, but the calculation of these rates was very likely flawed. Due to these rates possibly being much higher than in reality, unstable conditions occurred in the model for any significant release of ISA, preventing the numerical integration performed by BOXMOX from completing successfully. It was also noted that HCl was defined as being a fixed concentration in the .spc file, which possibly contributed to the unstable conditions.

By using the reaction flux plotting script or similar, it could be beneficial to trace key species and the species that are their main sources of production and loss to see if there is an inconsistency or a process that is not agreeing with realistic atmospheric chemistry.

Project schedule and internship learning

The project was for six weeks with 37.5 hours of work per week. I worked in-person in the ACRG building located by the Department of Chemistry, Cambridge. My normal work day was from 9am to 5:30pm with an hour of break time, which included lunch. The project was overseen by Prof. Alex Archibald, and I was supervised on a day-to-day basis by Dr. Laura Stecher.

I succeeded in learning how to use the modelling software alongside learning from scratch the language it used, Fortran. I also became much more proficient in reading, understanding, and making notes from literature. Furthermore, I learnt about many of the chemical cycles within the atmosphere and how they interlock with one another, building on my knowledge from lecture content.

I struggled with debugging the modelling software as there was little information about it online and many of the errors were vague, however I overcame this by being persistent in trying different solutions and approaches. It was also difficult to find a comprehensive set of equations for aqueous phase iron chemistry, along with finding the rates of these reactions. This was partially overcome by assuming rates for some reactions based on knowledge of similar reactions, however with more time available it may have been possible to find experimental values for the rates by conducting an in-depth literature review.

If I were to conduct this research project again, I would focus on fully understanding why the initial model gave results so different to those in the literature before beginning to implement the aqueous phase chemistry, as this would reduce the number of pre-existing issues within the updated model alongside allowing me to understand the processes occurring to a greater extent.

At the end of my internship I provided Prof. Archibald and Dr. Stecher with a full report on my findings. I also provided them with a short description of how I set BOXMOX up and common errors that I encountered so that any future research conducted using it would have a reference guide, as I found this process to be very time consuming during my internship. I also included the scripts I used to calculate and plot reaction fluxes so that they could be used in future research if required.

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