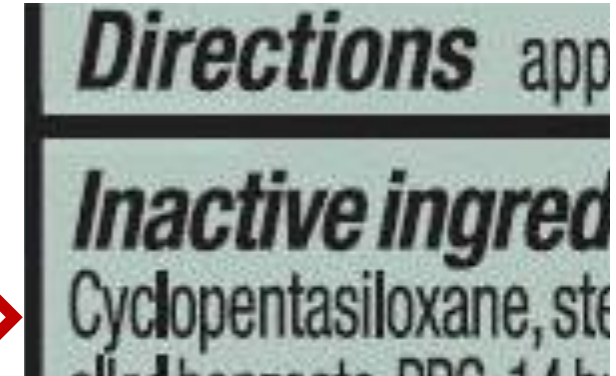
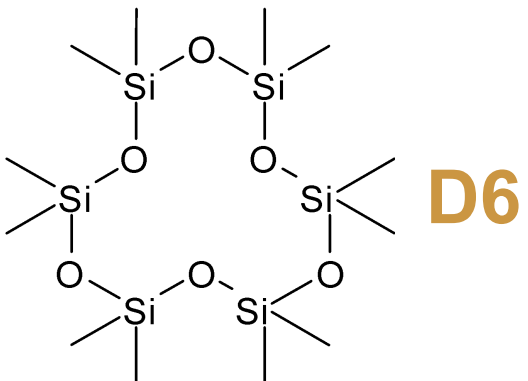
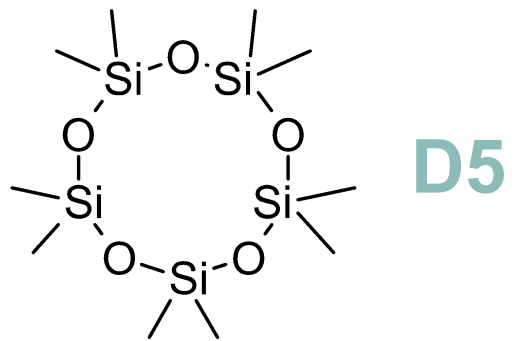
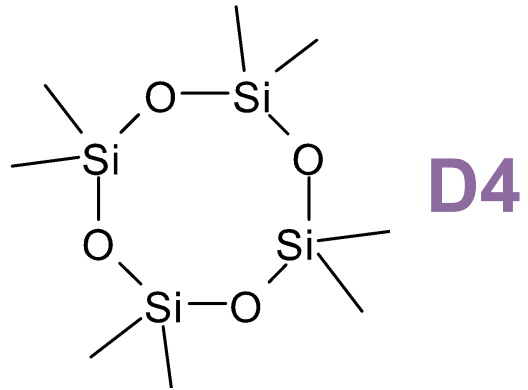
A world map with a color scale overlay representing atmospheric concentrations of Volatile Methyl Siloxanes. The map shows higher concentrations (red and orange) in the Northern Hemisphere, particularly in North America, Europe, and East Asia, and lower concentrations (green and blue) in the Southern Hemisphere. A semi-transparent grey box is overlaid on the map, containing the title and authors.

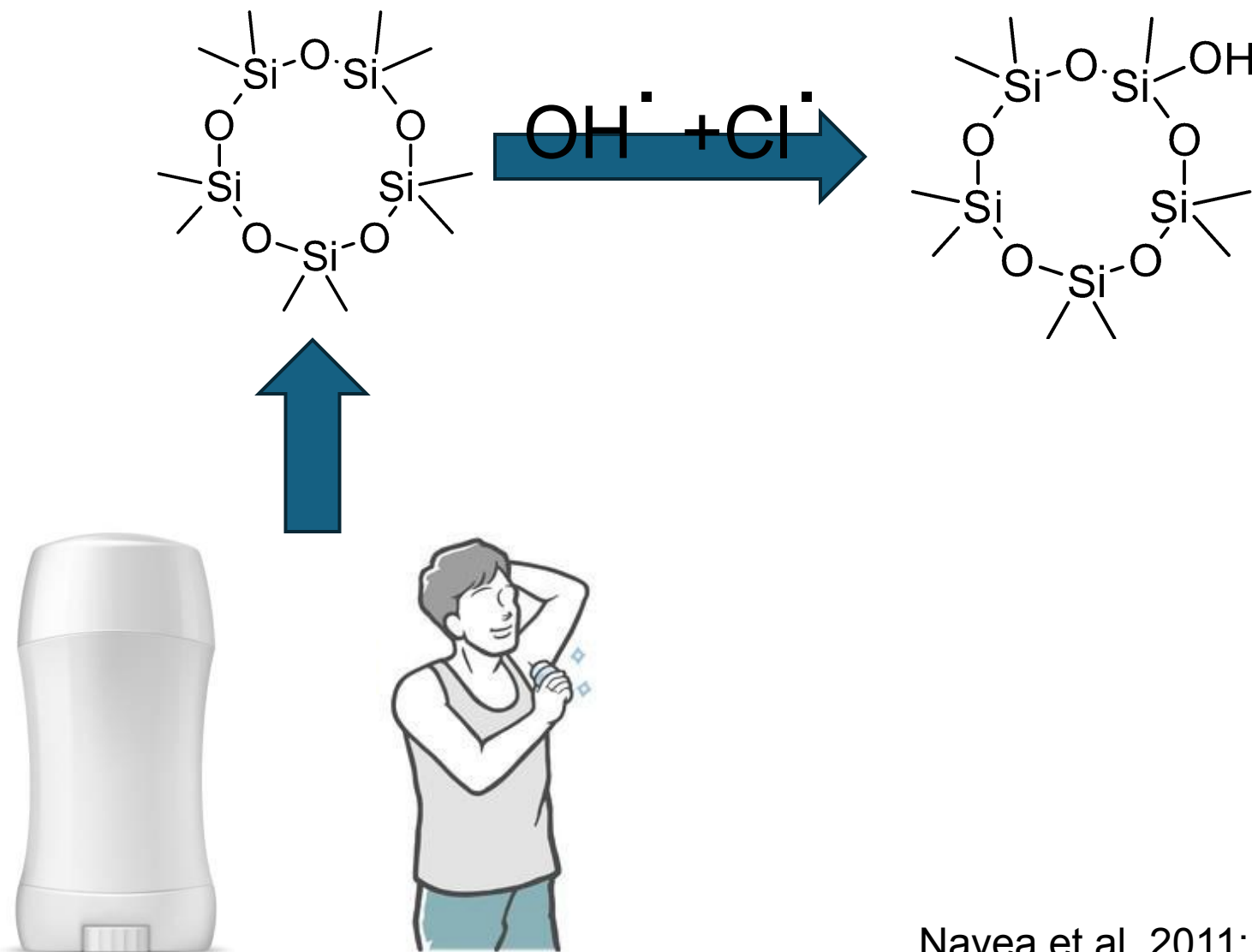
Exploring the impact of chlorine oxidation and temperature dependent reaction rates on the atmospheric lifetimes and concentrations of Volatile Methyl Siloxanes in CESM.

Christopher Brunet, Saeideh Mohammadi, Behrooz Roozitalab, Charles Stanier, Keri Hornbuckle

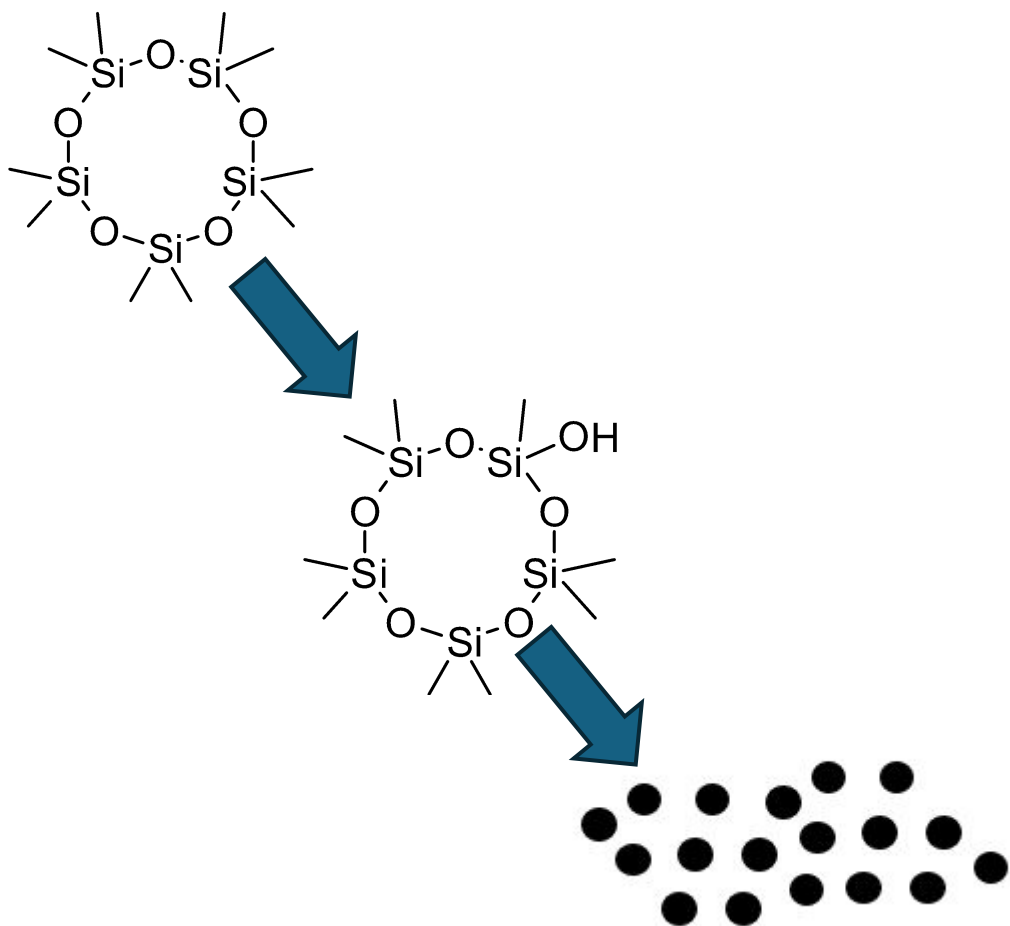
Volatile Methyl Siloxanes are synthetic organosilicons widely found in consumer items and, in particular, personal care products.



Due to their high volatility, and inclusion in these products, over 90% of VMS compounds are emitted into the atmosphere where they undergo oxidation by hydroxyl and chlorine radicals with lifetimes on the order of 5-10 days.



VMS have gained considerable attention in the past two decades from both the scientific and regulatory community due to their relatively long atmospheric lifetimes, ability to form secondary organic aerosols (SOA) and their potential to serve as tracer compounds for other volatile organic compounds (VOC) and their SOA.



ANNEX XV RESTRICTION REPORT

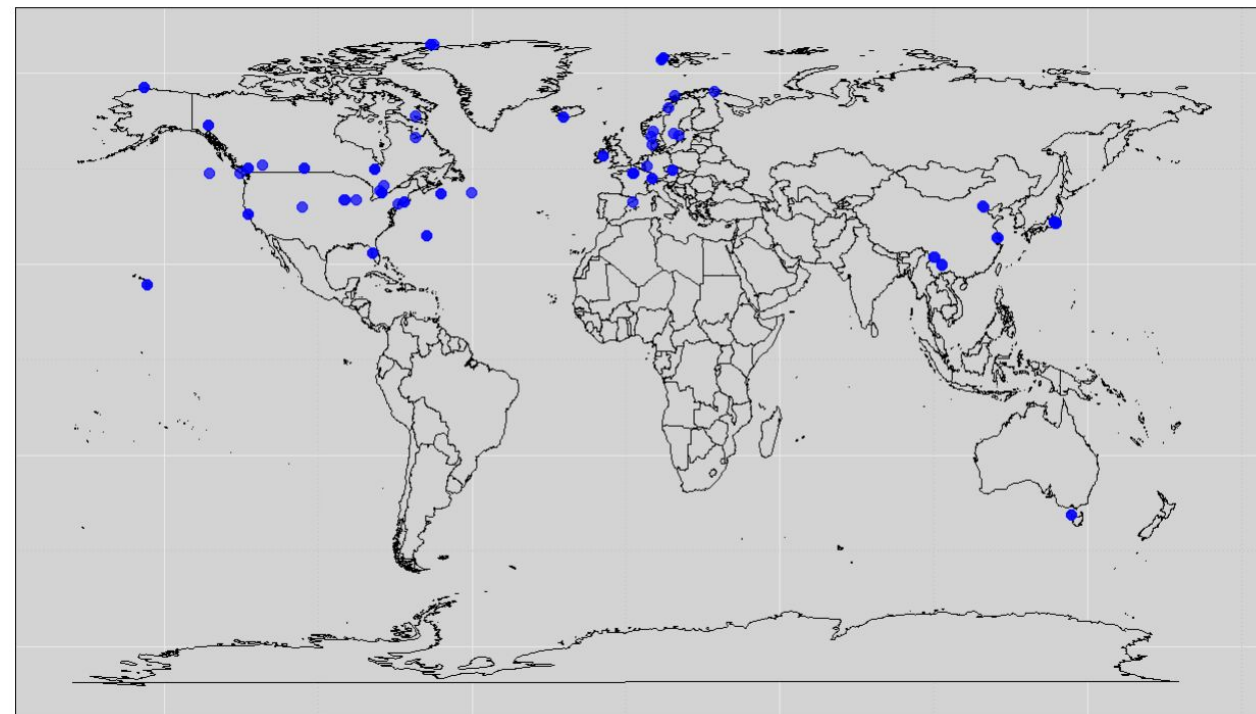
PROPOSAL FOR A RESTRICTION

SUBSTANCE NAME(S):	Octamethylcyclotetrasiloxane (D4) Decamethylcyclopentasiloxane (D5) Dodecamethylcyclohexasiloxane (D6)
EC NUMBER(S):	209-136-7, 208-764-9, 208-762-8
CAS NUMBER(S):	556-67-2, 541-02-6, 540-97-6

Our group and other researchers have conducted a number of field campaigns aimed at understanding the atmospheric behavior of VMS.

Concentrations of Volatile Methyl Siloxanes in New York City Reflect Emissions from Personal Care and Industrial Use

Christopher E. Brunet, Rachel F. Marek, Charles O. Stanier, and Keri C. Hornbuckle*

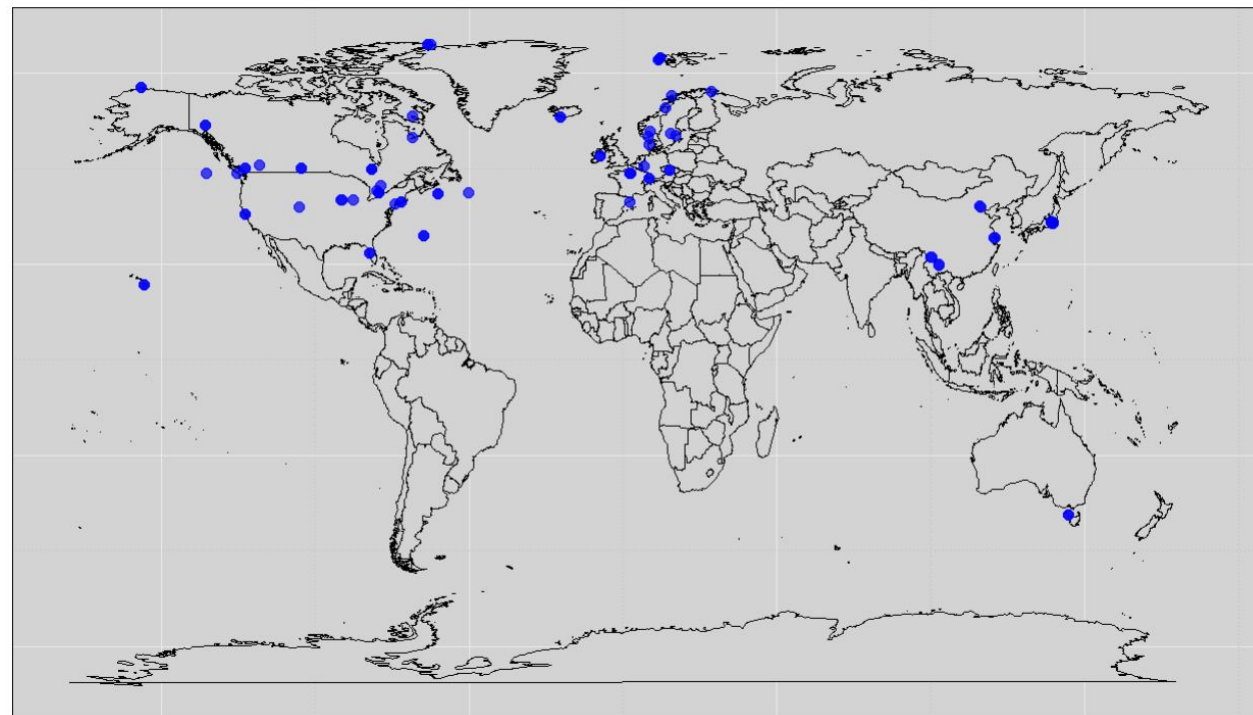


Locations of Previous Field Studies

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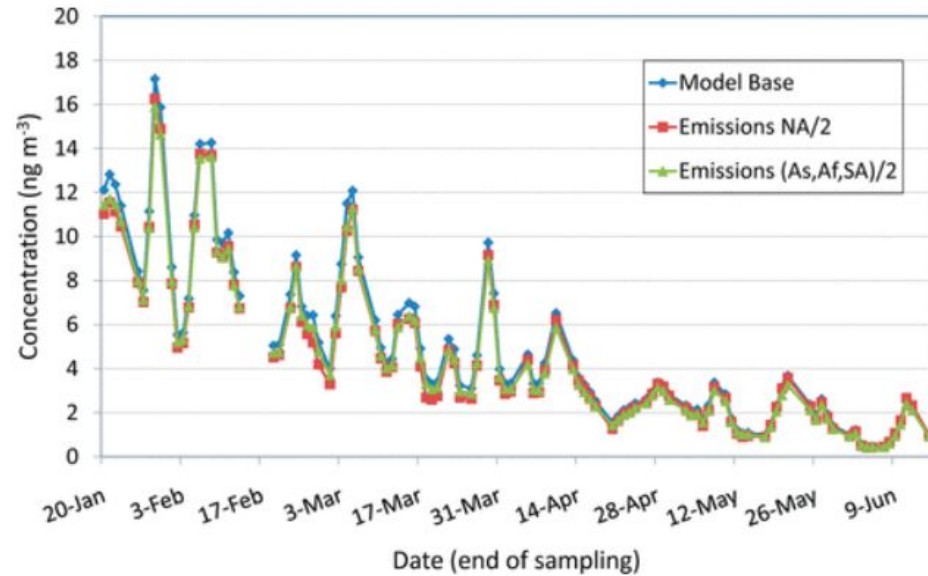


Locations of Previous Field Studies

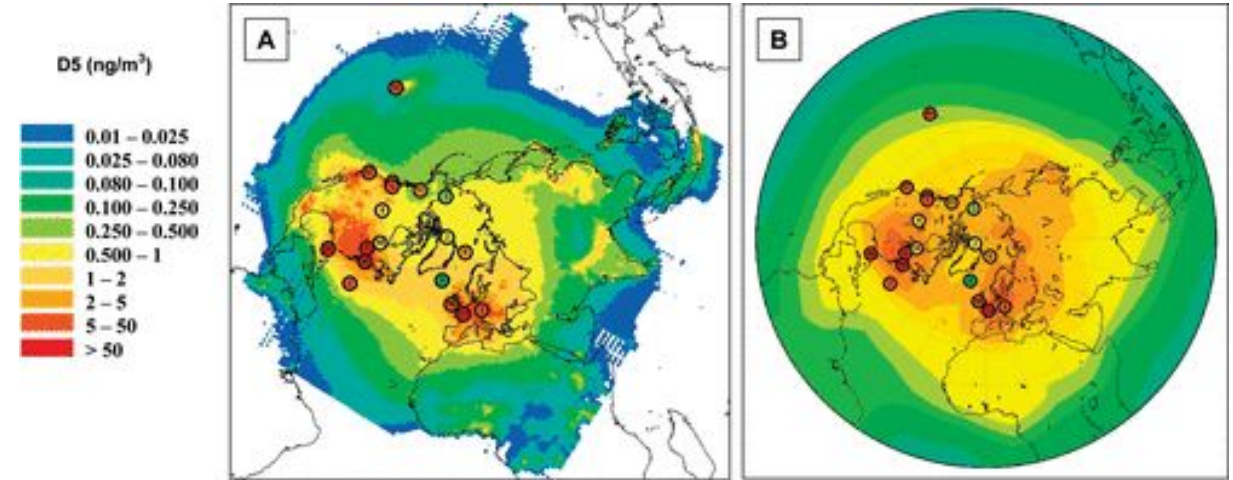
But, even after these studies there a number of important questions which can only be addressed by atmospheric modeling.

A number of previous atmospheric-transport models have been used to estimate the atmospheric concentrations of VMS.

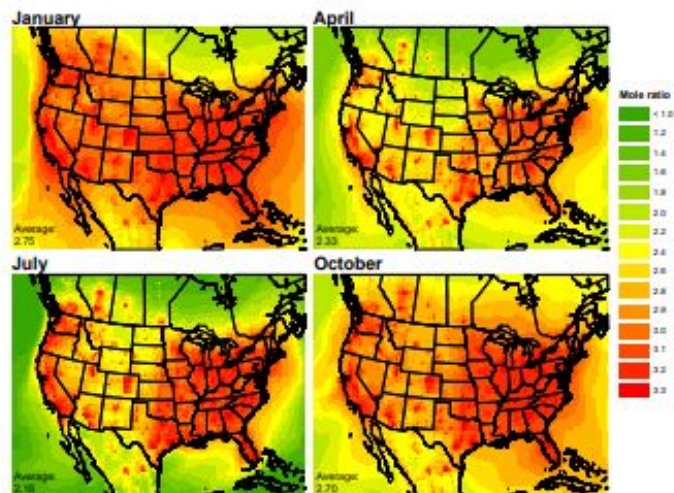
McLachlan et al. 2010 | Danish Eulerian Hemispheric Model



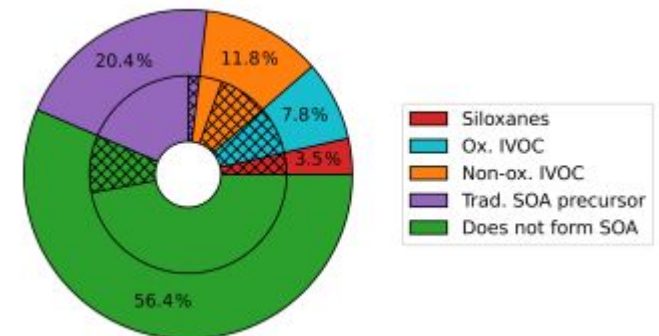
Genauldi et al. 2011 | DEHM+BETR



Janecek et al. 2017 | Community Multiscale Air Quality

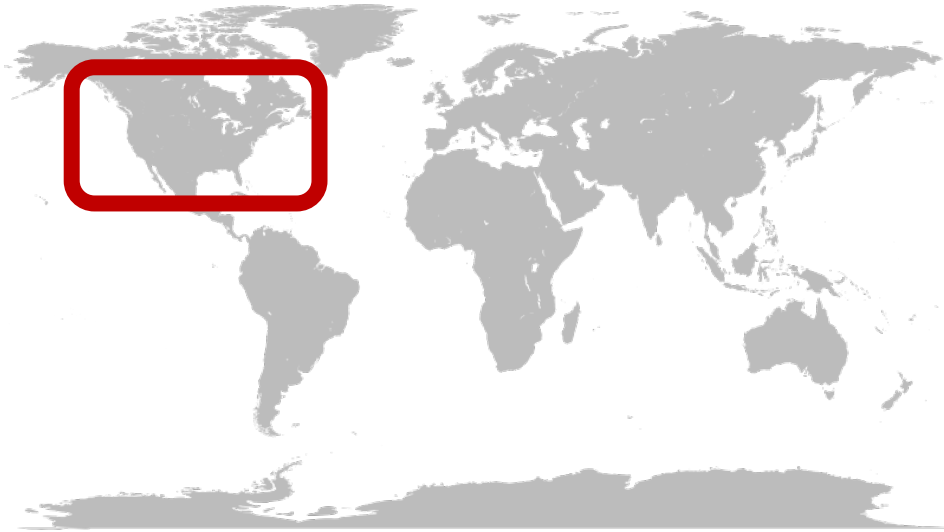


Pennington et al. 2021 | Community Multiscale Air Quality

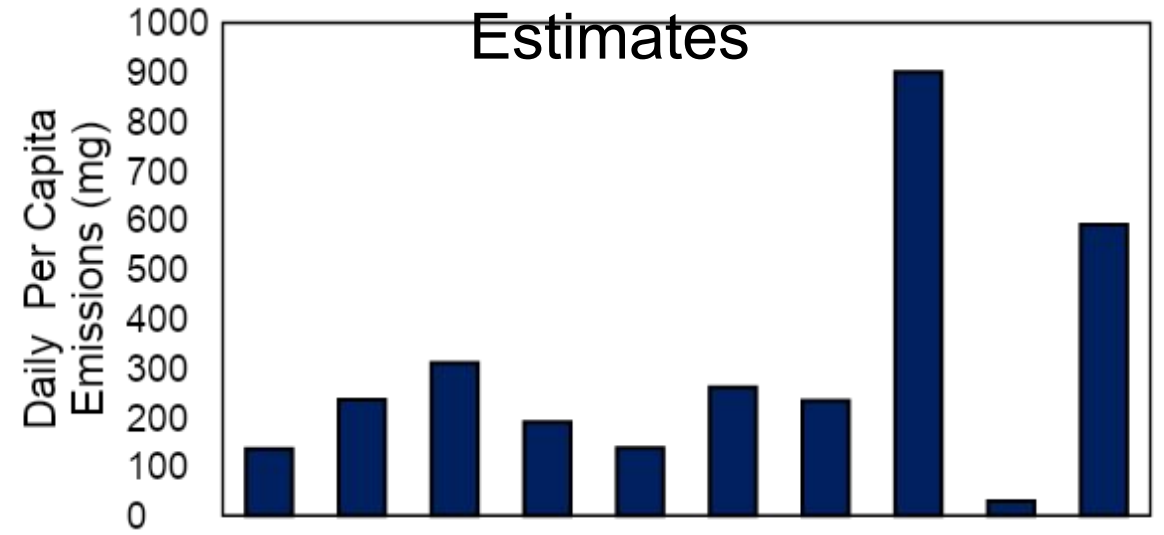


However, these models have been limited in a number of keyways which either introduces uncertainty into their results or makes it impossible to answer certain scientific questions.

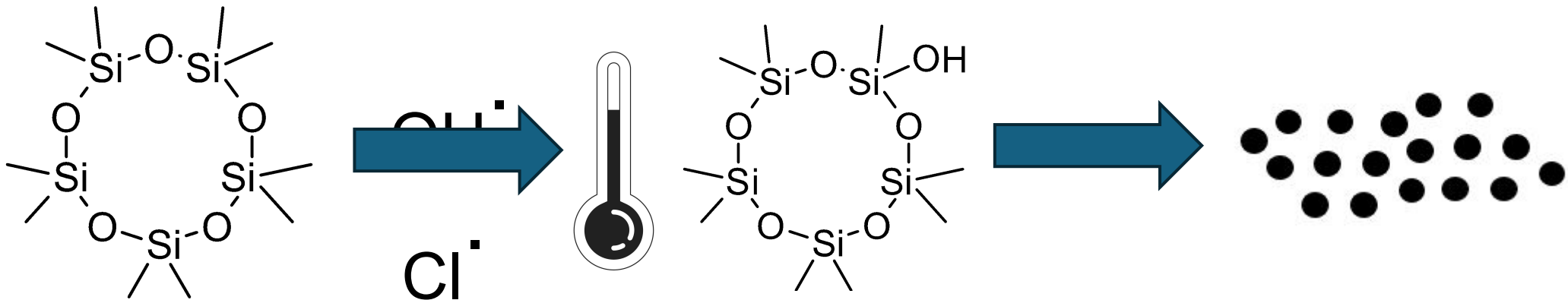
Limited Geographical Domain



Wide Range of Per Capita Emissions Estimates

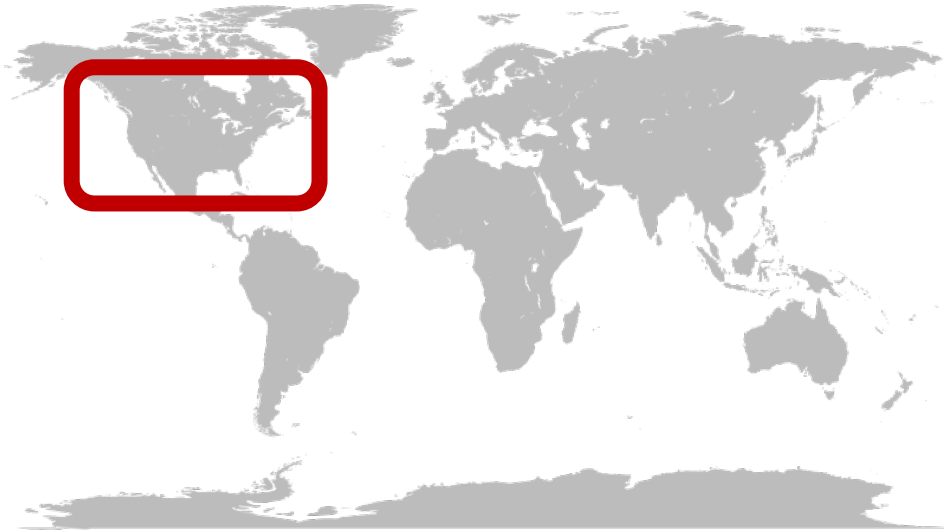


Chemical mechanisms did not fully capture VMS oxidation processes.

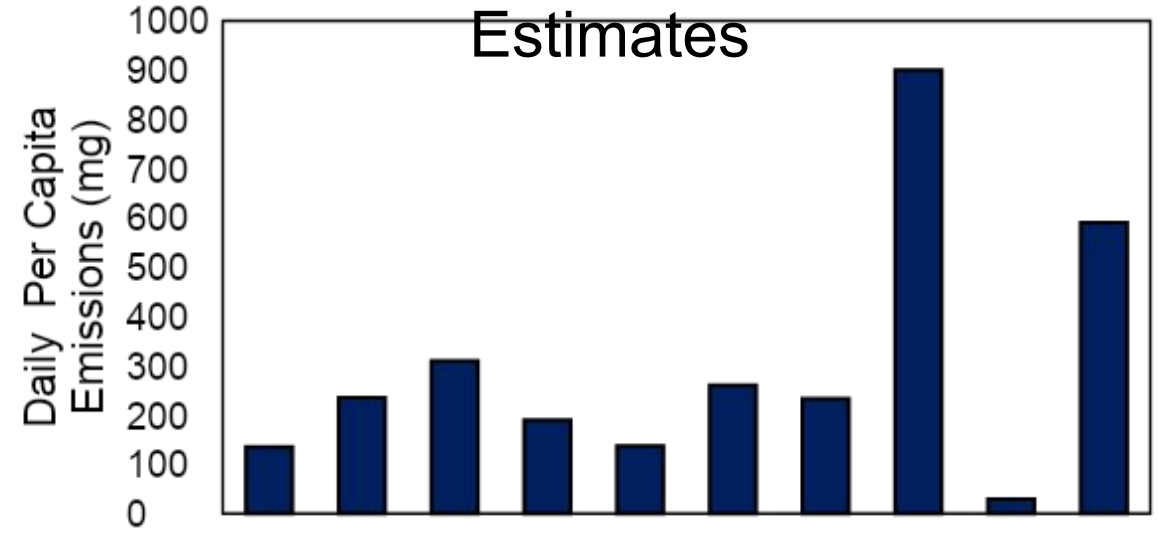


However, these models have been limited in a number of keyways which either introduces uncertainty into their results or makes it impossible to answer certain scientific questions.

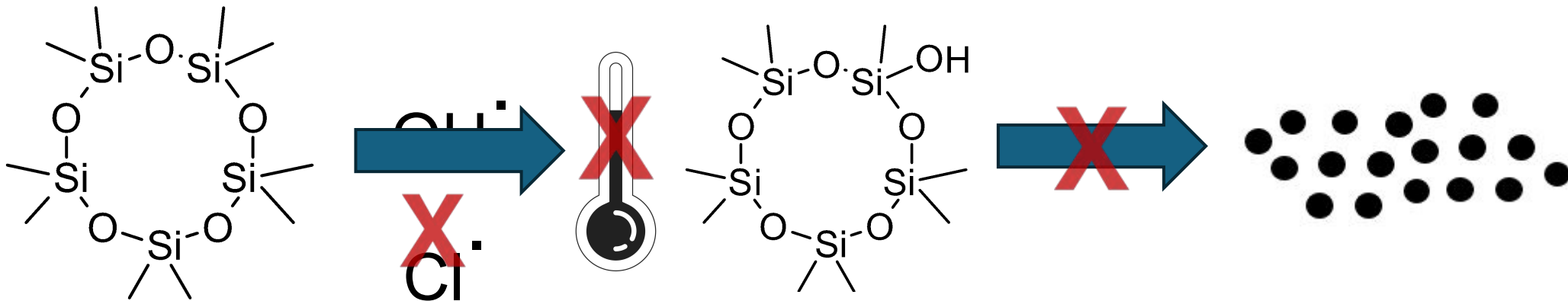
Limited Geographical Domain



Wide Range of Per Capita Emissions Estimates



Chemical mechanisms did not fully capture VMS oxidation processes.



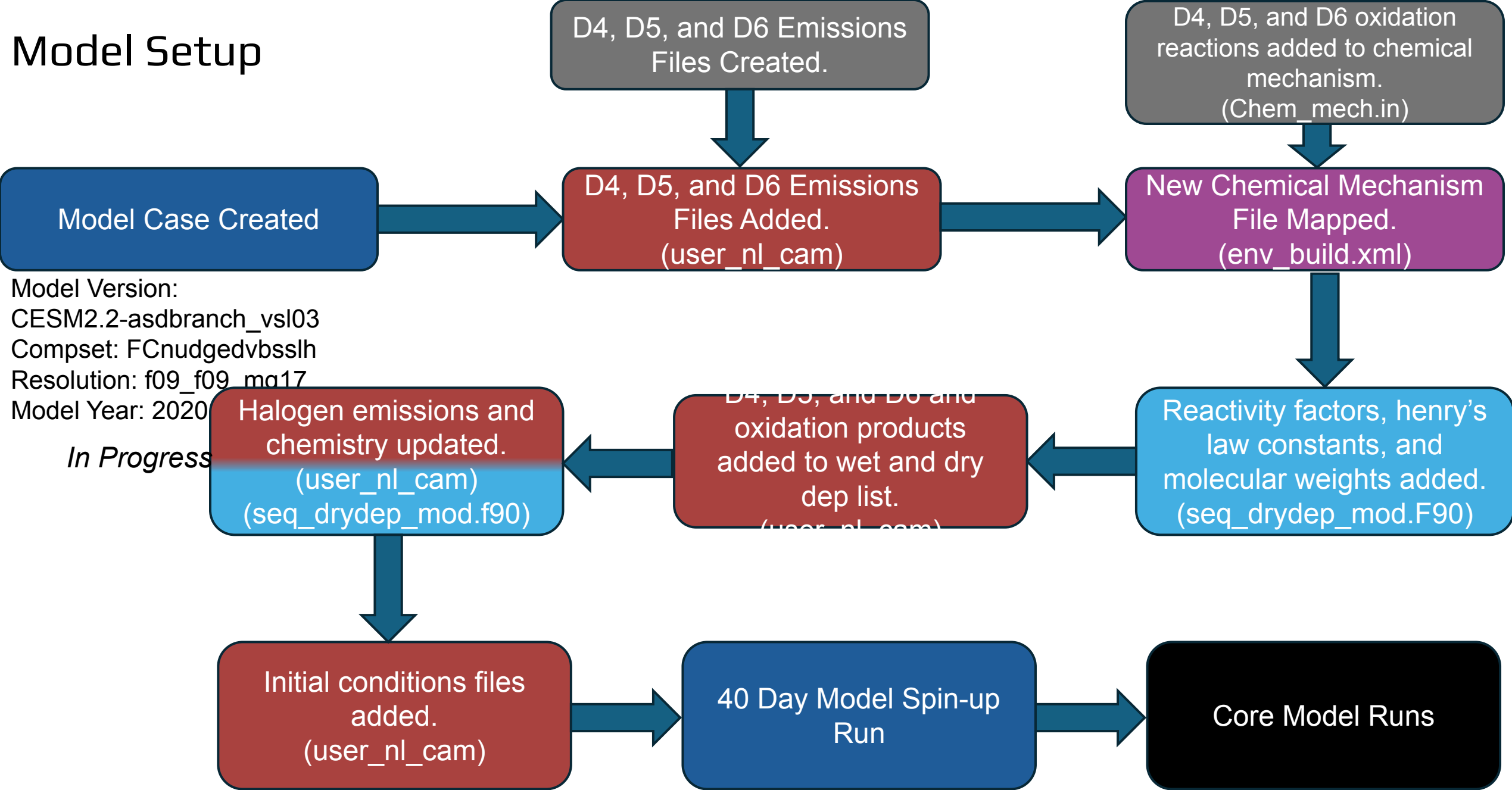
Our goal was to create a global atmospheric model of 3 VMS compounds (D4, D5, and D6) in CESM using the best currently available knowledge about their per capita emissions, physical parameters, and reaction rates and use it to asses...

1. How does including temperature dependence influence the predicted concentrations and lifetimes of VMS?
2. What is the impact of chlorine oxidation on the atmospheric concentrations and lifetimes of VMS?
3. How well can we predict the range of VMS concentrations outside of the United States by extrapolating the U.S. per capita emissions rates and using population density as the only predictive factor for emissions?

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Model Setup



Experimental Setup

4-Core Models Runs were performed with all parameters kept the same except for the chemical mechanism used.

Run 1:

Chlorine Oxidation: **No**

Temperature Dependence:
No

Simple

Run 2:

Chlorine Oxidation: **No**

Temperature Dependence: **Yes**

T

Run 3:

Chlorine Oxidation: **Yes**

Temperature Dependence: **No**

*Cl (in
progress)*

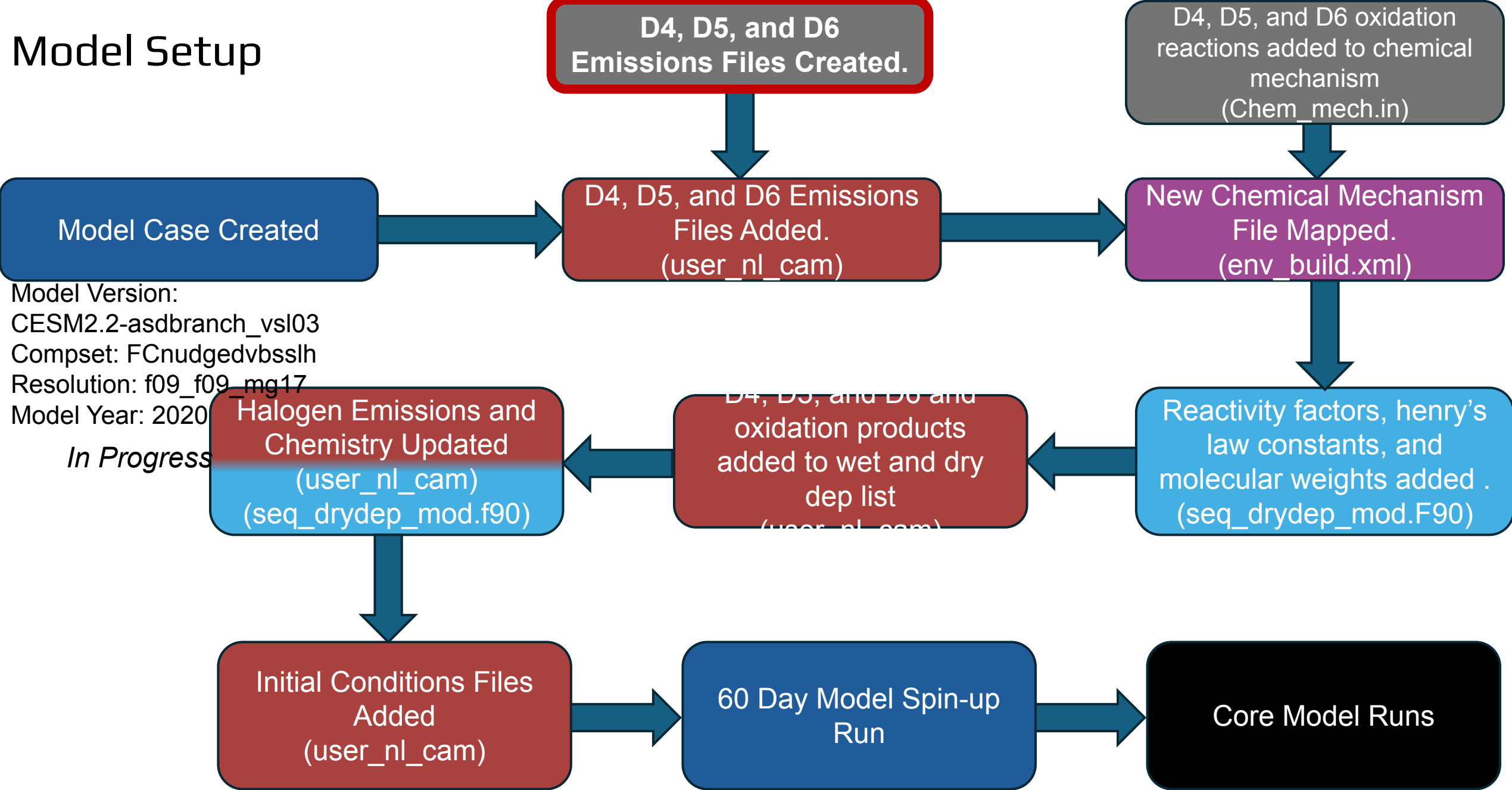
Run 4:

Chlorine Oxidation: **Yes**

Temperature Dependence: **Yes**

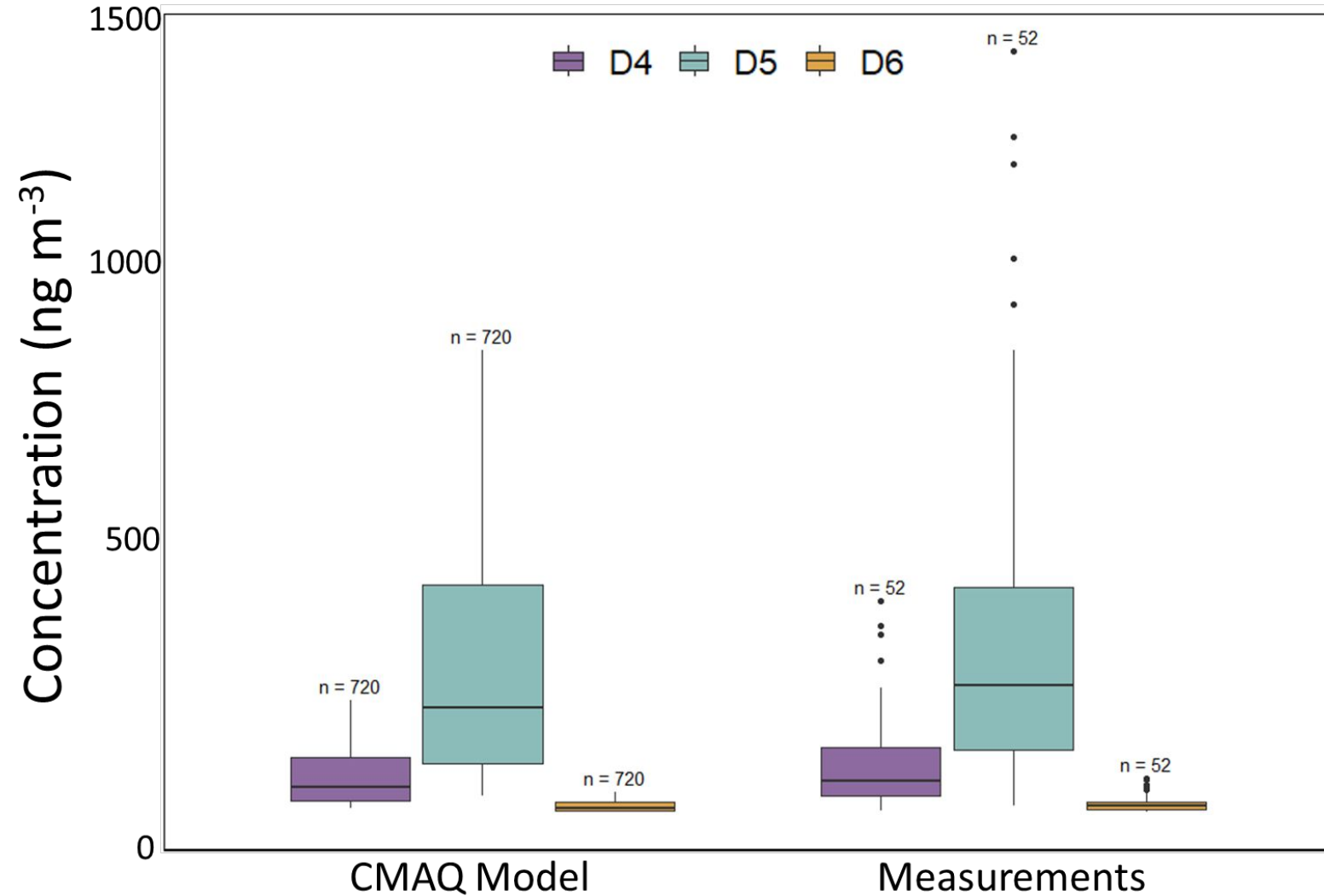
*Cl+T (in
progress)*

Model Setup



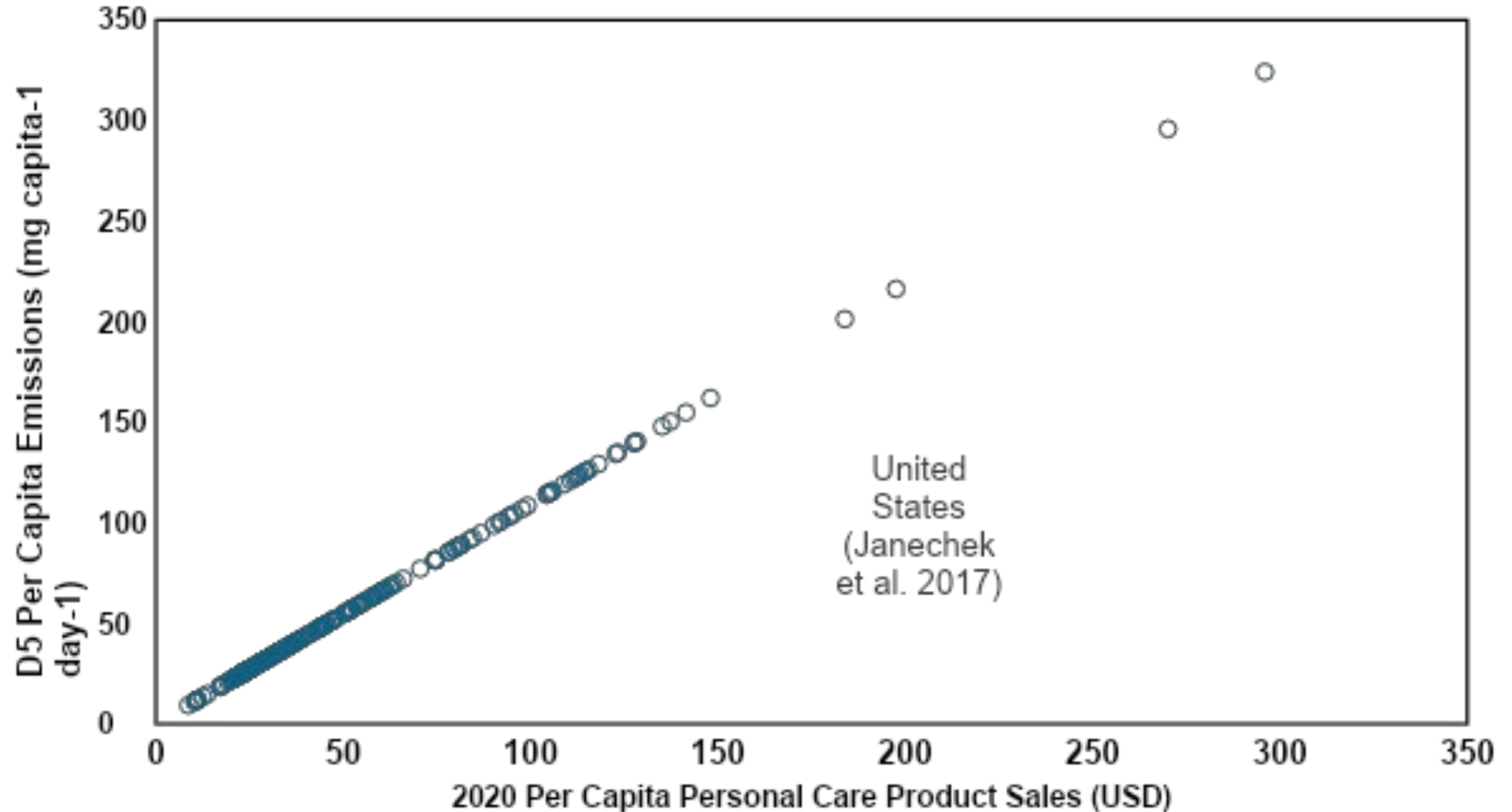
Creation of VMS Emissions Files

Comparisons between the Janecek et al. 2017 CMAQ model and field measurements suggest that the Per Capita Emissions rates for the United States used in this model are likely the best available.



Creation of VMS Emissions Files

Per capita emissions rates for the rest of the world were calculated by normalizing the U.S. per capita emissions rates by country specific personal care product sales revenue.



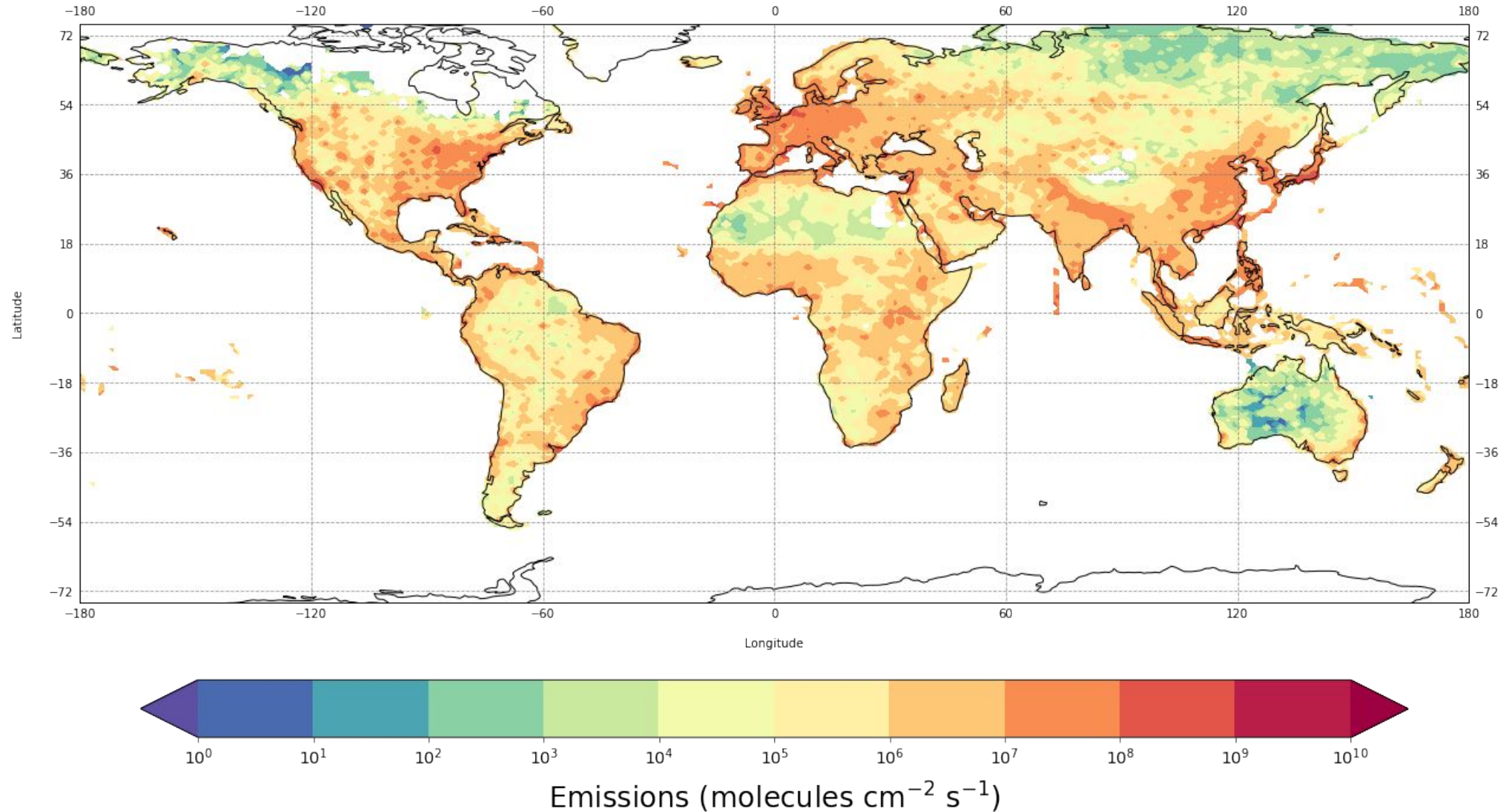
Creation of VMS Emissions Files

1x1km emissions estimates were generated by combining population density data compiled from WorldPop.org with these per capita emissions rates.

	$\begin{array}{c} \text{Per Capita Emission Rate} \\ \times \\ \text{Grid Cell Population} \\ \text{Density} \\ = \\ \text{Emissions} \end{array}$		

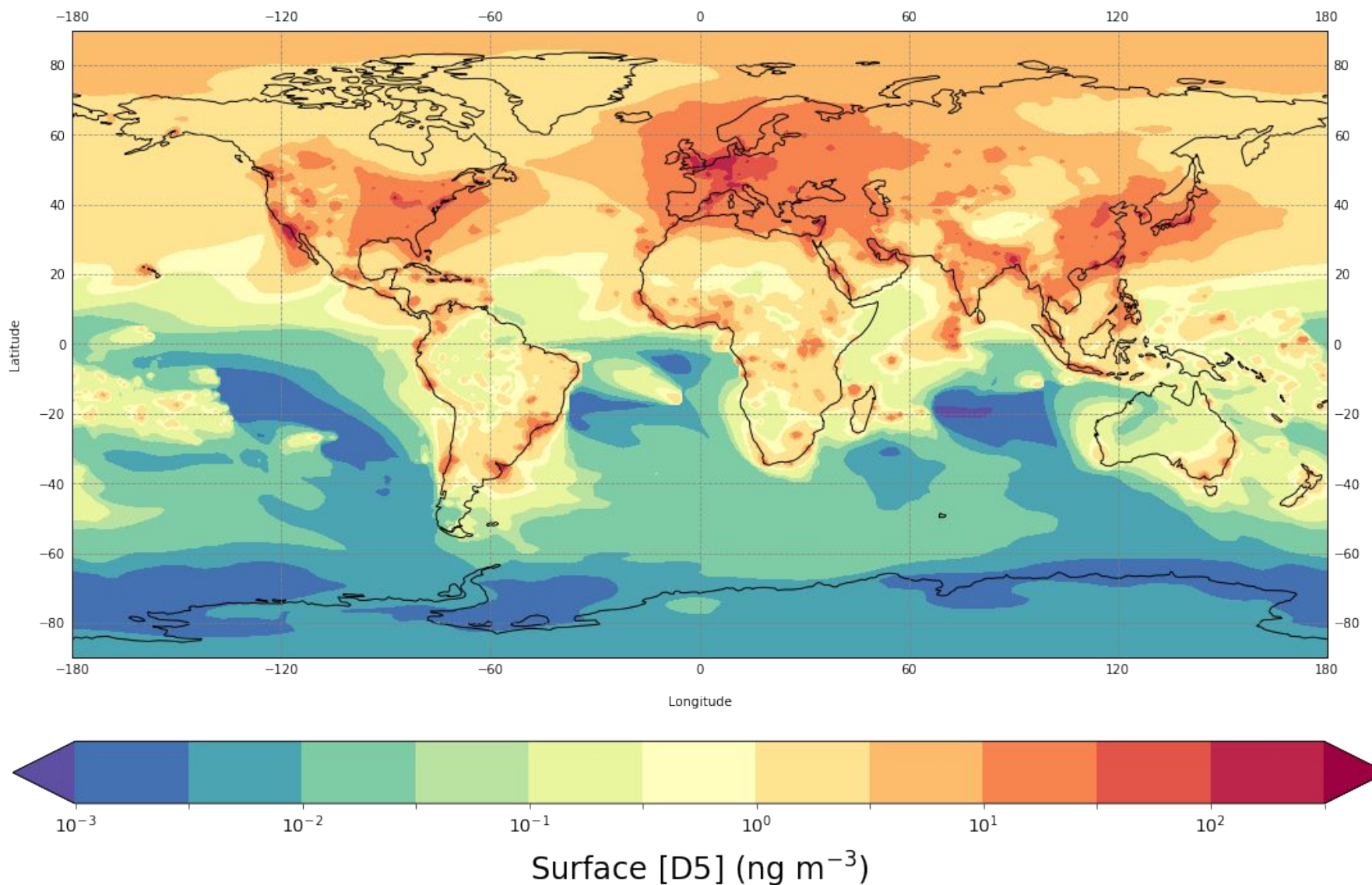
Creation of VMS Emissions Files

1x1 km emissions estimates were used to generate a CESM emissions file by aggregating all 1x1 km emissions that fell within each f09_f09_mg17 resolution grid cell. At this time, emissions are time invariant.

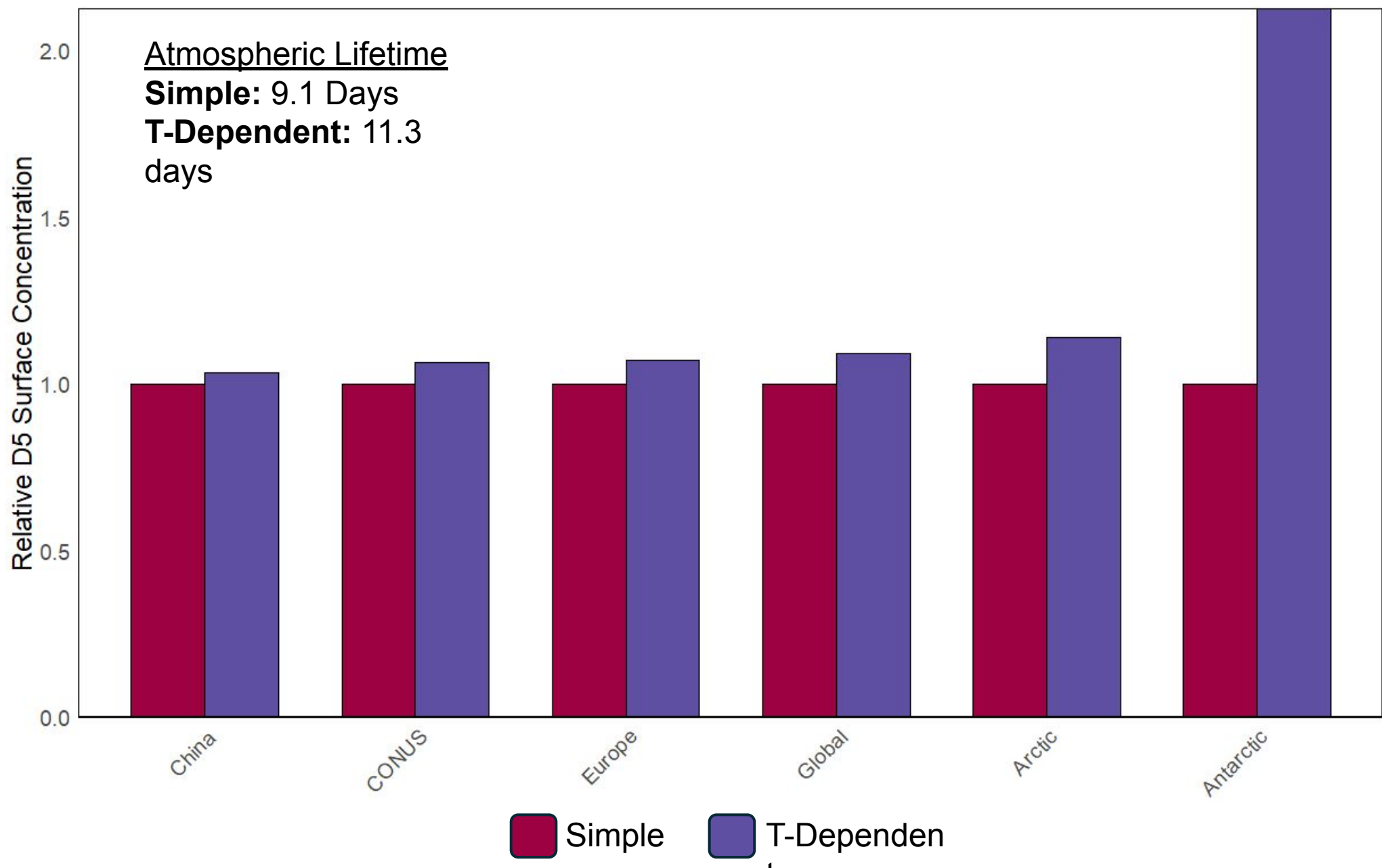


Initial (Very Preliminary) Results

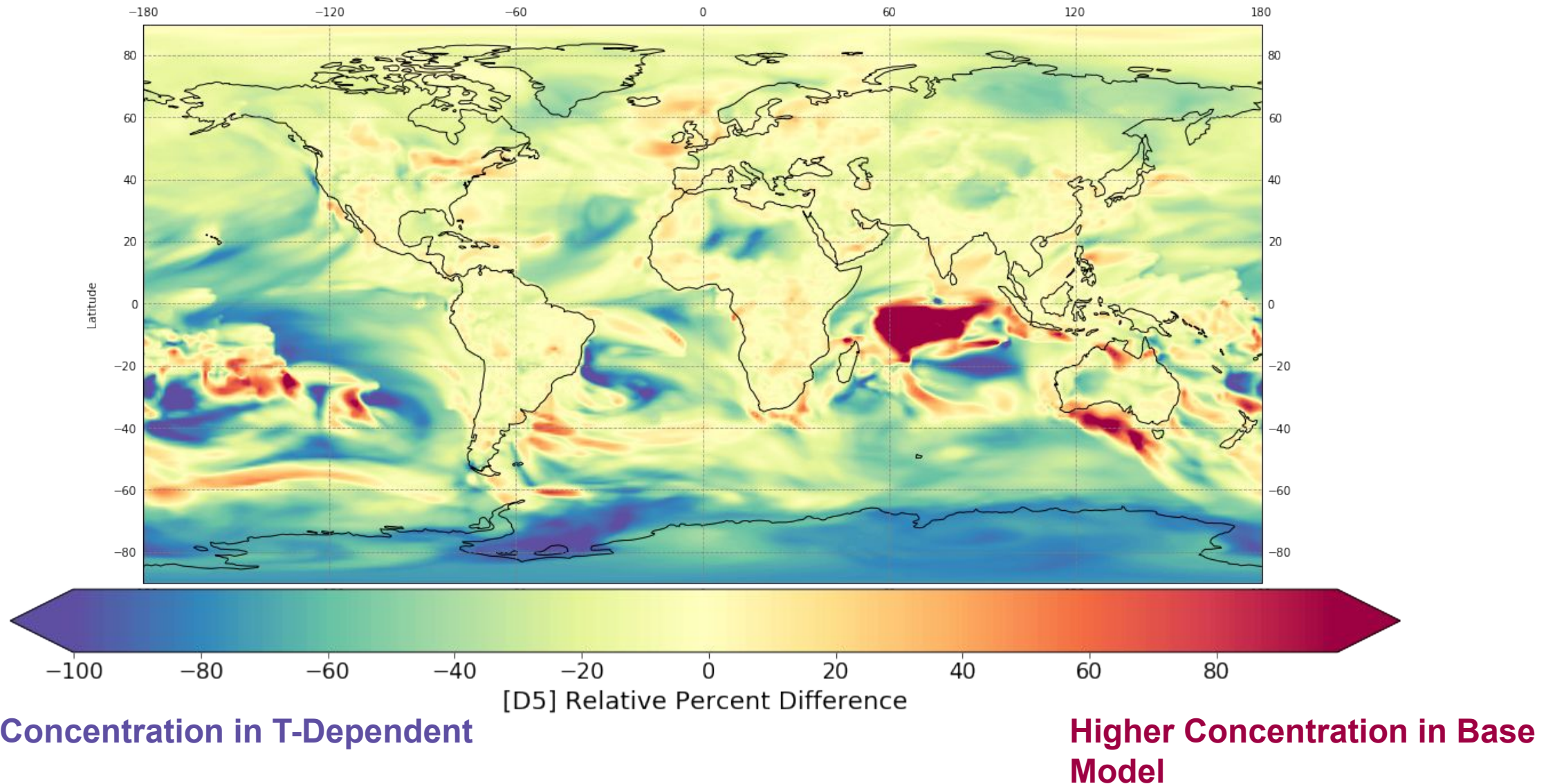
Model results for February of 2020 follow the expected concentration distribution with elevated concentrations occurring near densely populated areas and higher background concentrations in the northern hemisphere than the southern hemisphere. Peak concentrations in the range of 300-400 ng m⁻³ are comparable to previous field measurements.



The addition of temperature oxidation increased February D5 surface concentrations in all regions with larger differences observed in regions which are transport rather than emissions dominated.



However, changes were not uniform with some areas experiencing little no change and others increasing in concentration from the base model. Areas most effected were those that were dominated by long range transport that passed through areas with highly oxidizing conditions and large deviations in temperature from 298k.



Future Directions

- Longer model runs to give us a better idea of the impact of model changes during different seasons.
- Complete model runs with updated halogen chemistry to examine the impact of chlorine oxidation.
- Comparison of model results to concentrations measured in previous field campaigns.

Acknowledgements



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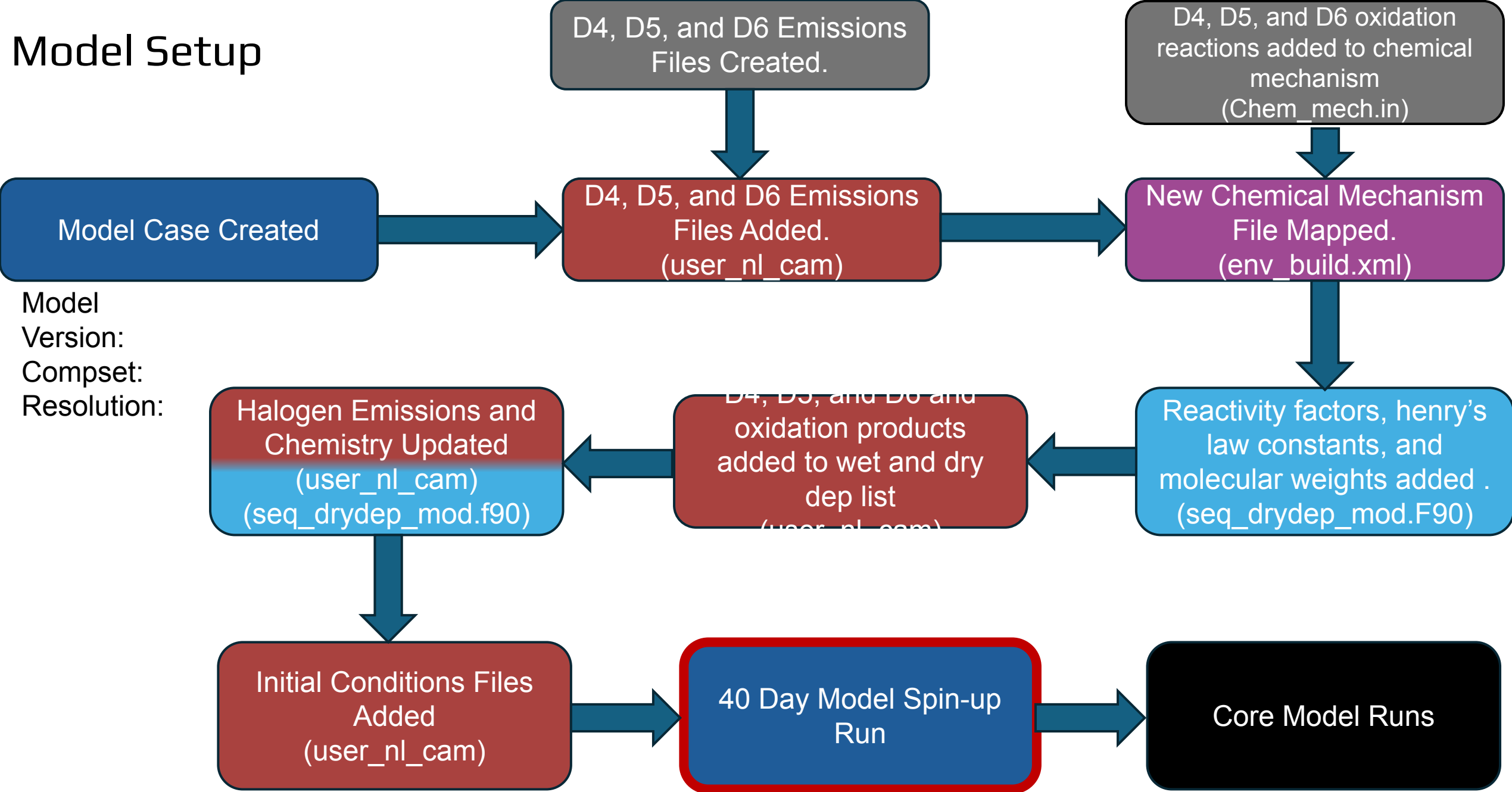
Stone Research Group

Elizabeth Stone
Josie Welker
Jeewani Meepage

Comments, Questions, Suggestions?

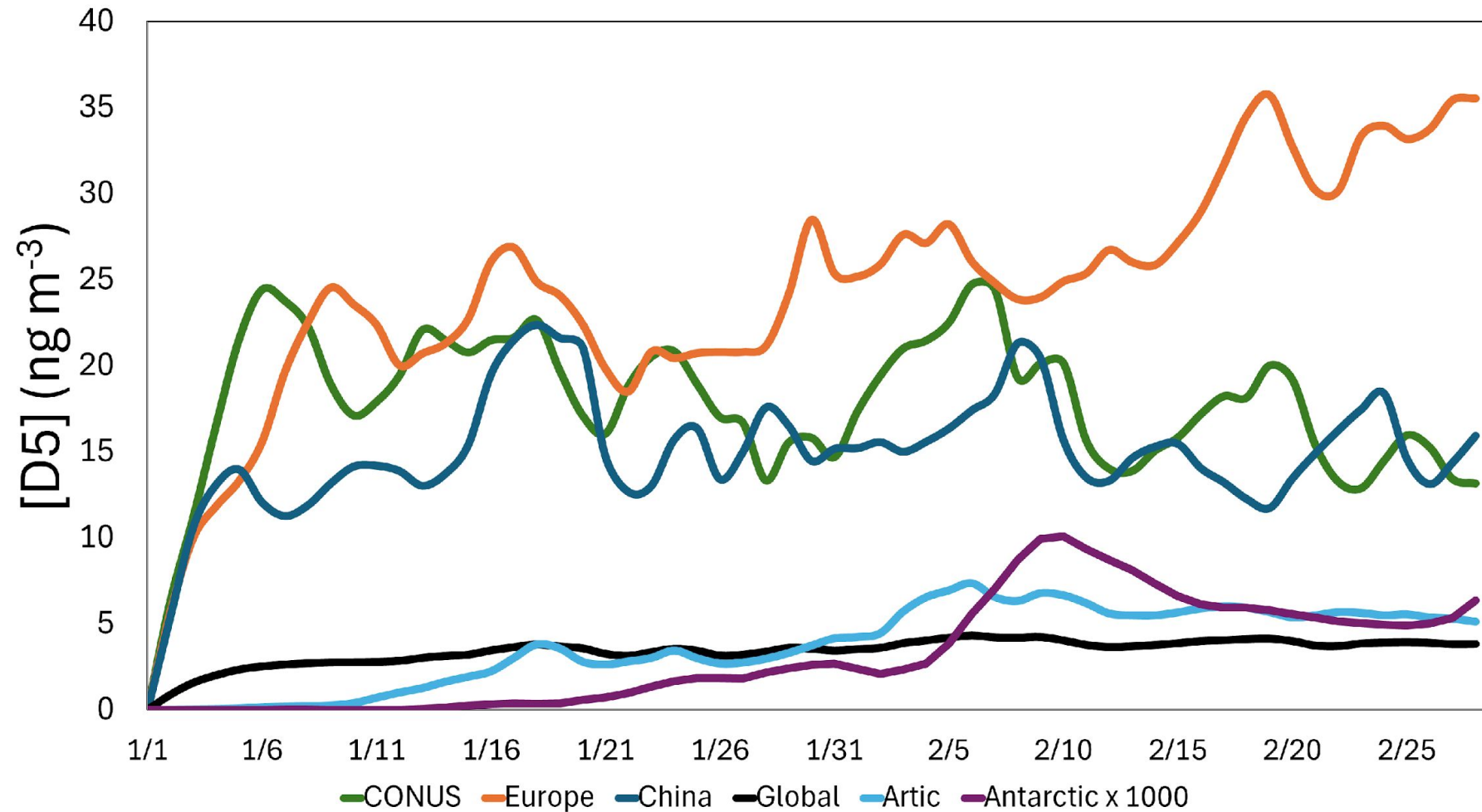
Additional Slides

Model Setup



Spin-Up Tests And Creation of Initial Conditions File

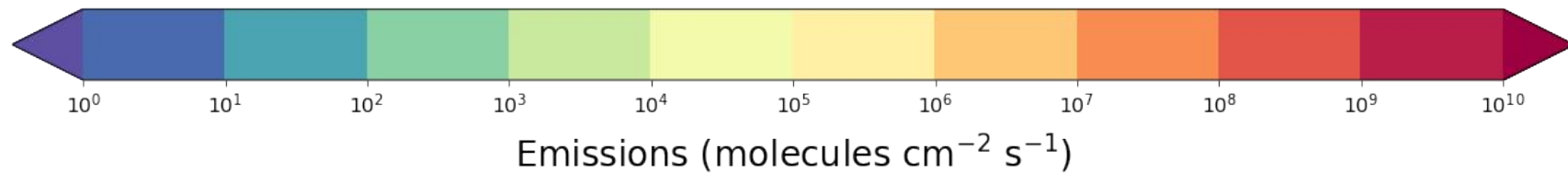
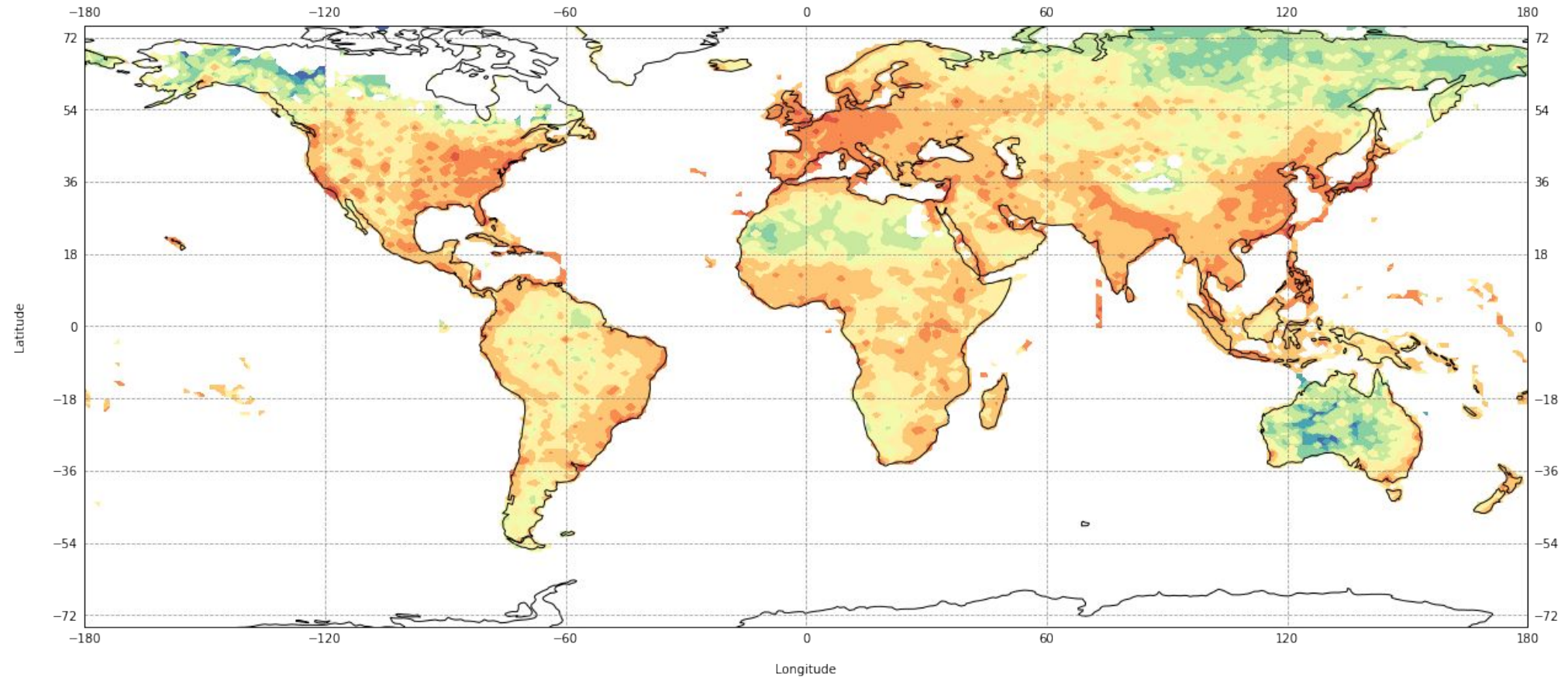
We conducted a model run with simple VMS chemistry (no Cl oxidation or T dependence) and initial conditions for all species except for VMS in order to determine how long it took concentrations to properly disperse. While surface concentrations in areas like the continental United States stabilized after approximately 5 days, concentrations in remote areas like the Arctic and Antarctic increased monotonically for up to 40 days.



The restart file from this run was used as the initial condition for all later runs.

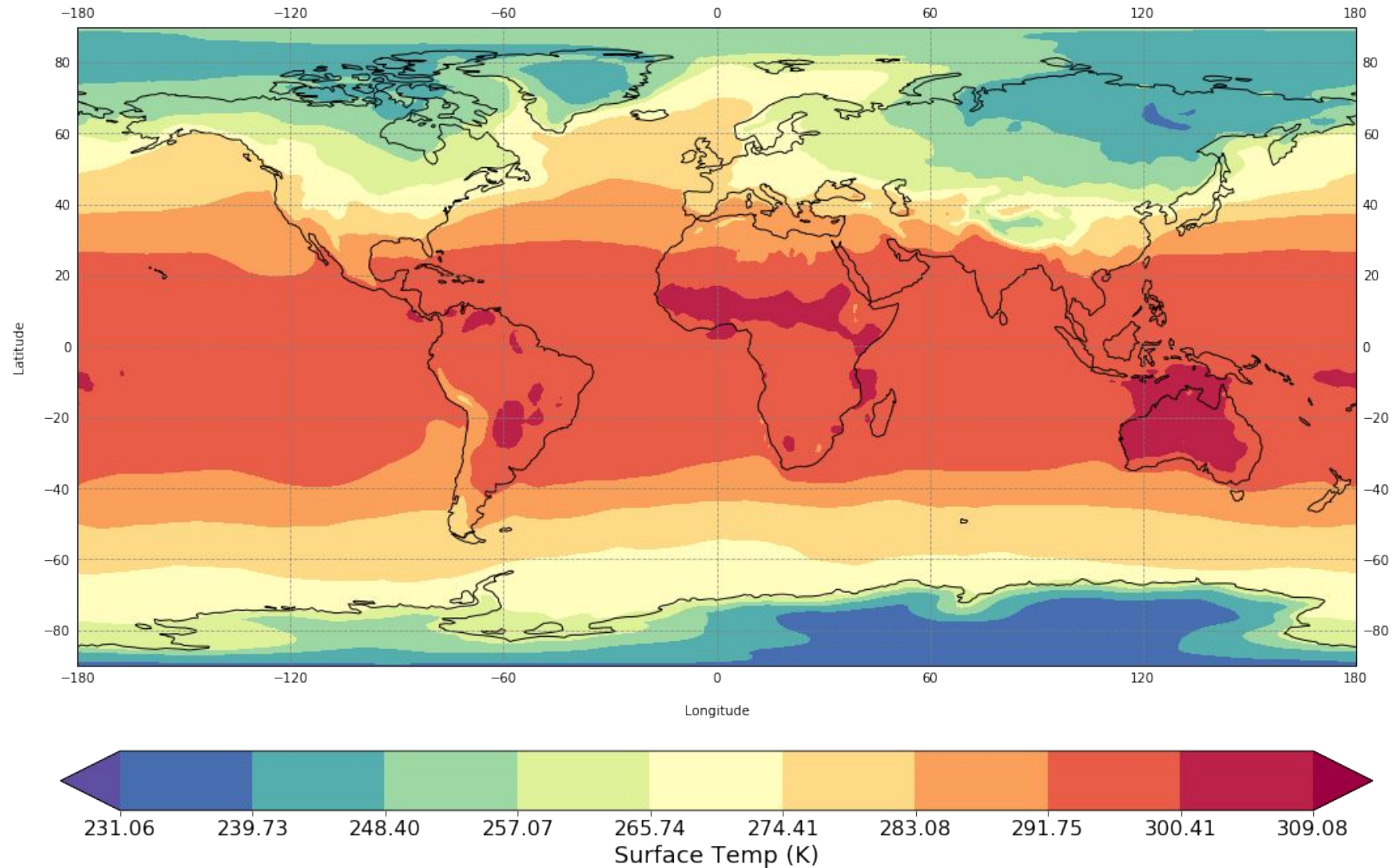
In order for large deviations between models to occur VMS must

1. Have sufficient time to undergo significant oxidation and...



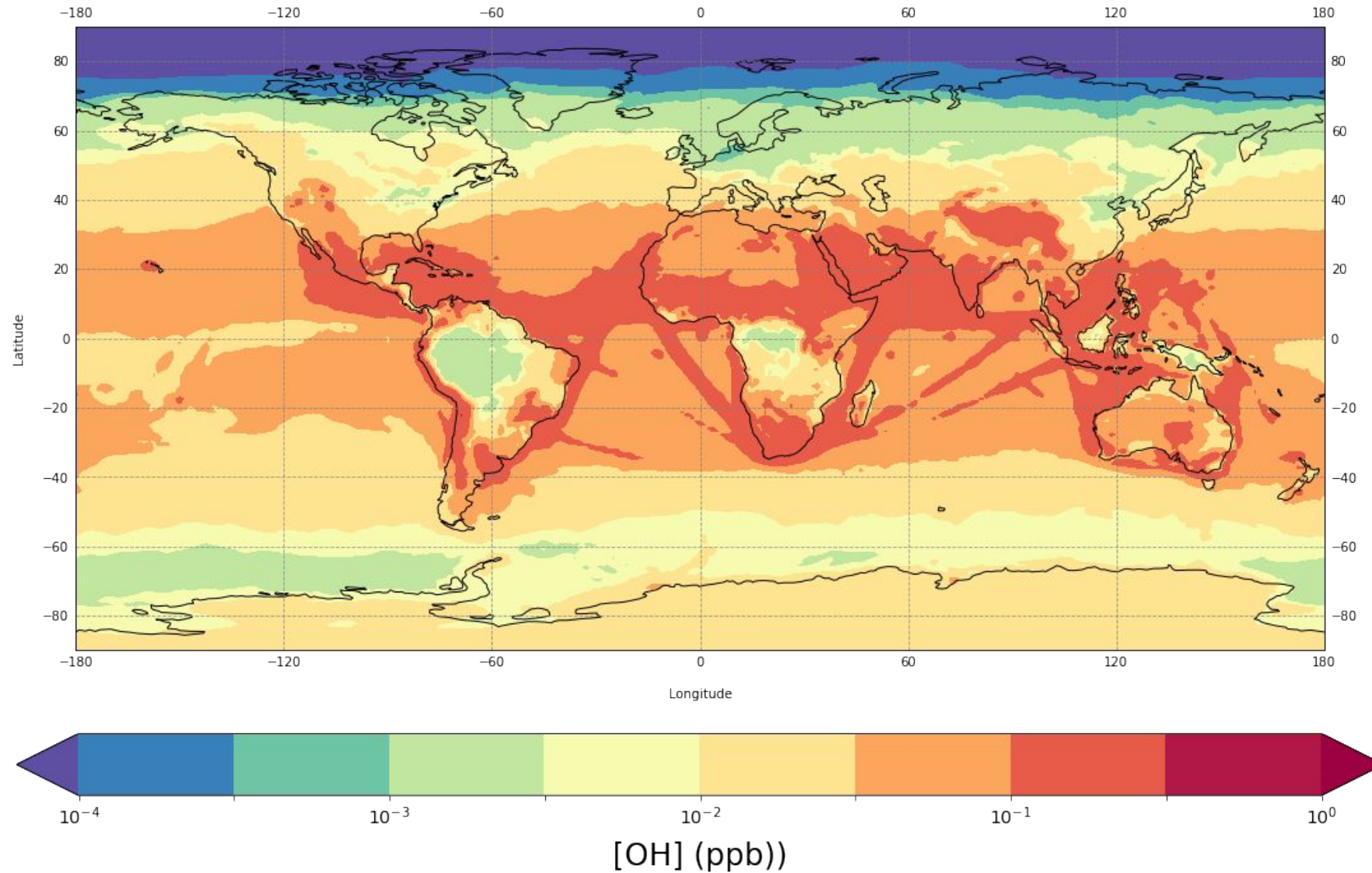
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2. Pass through a region with a large temperature deviation from 298k...

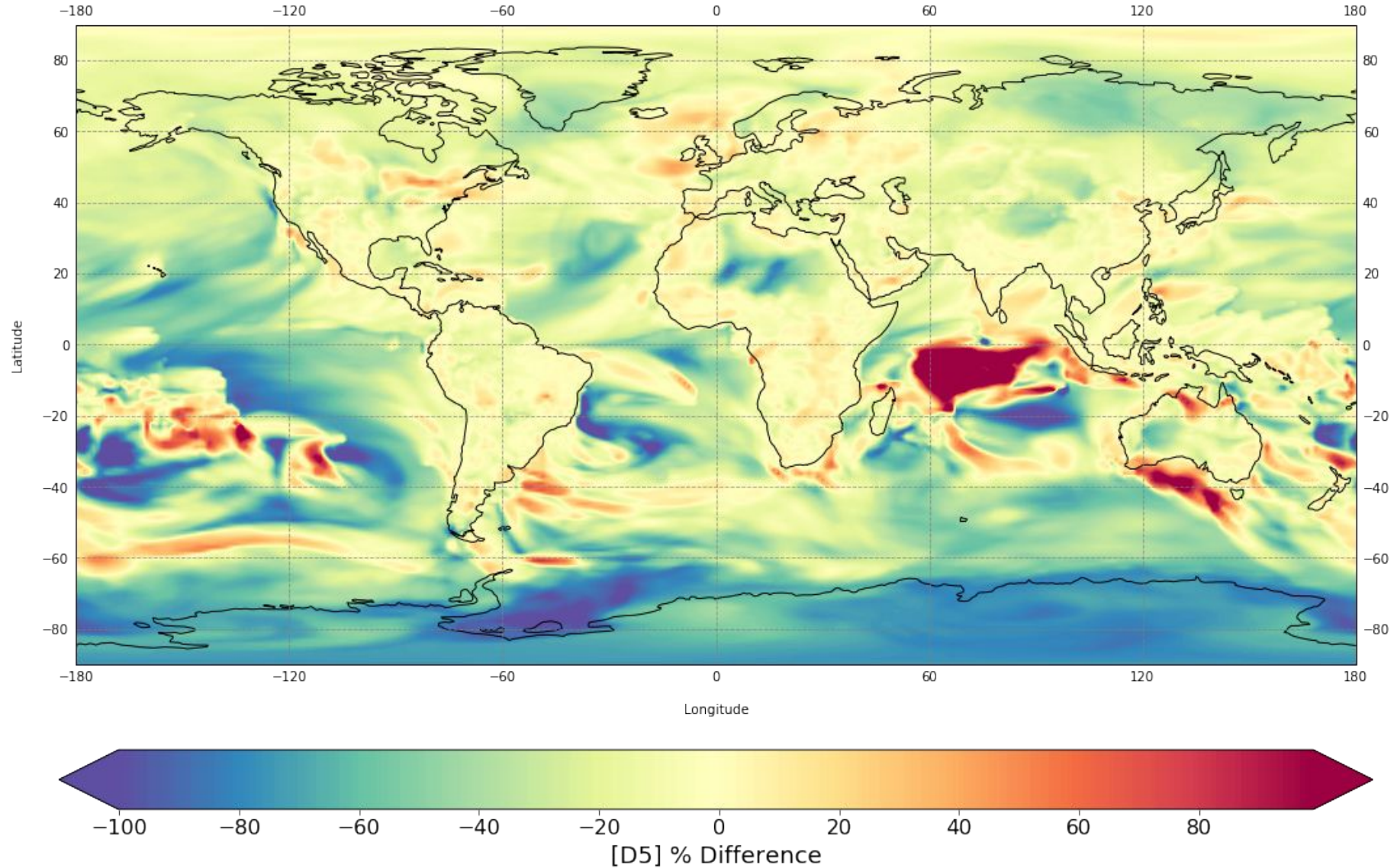


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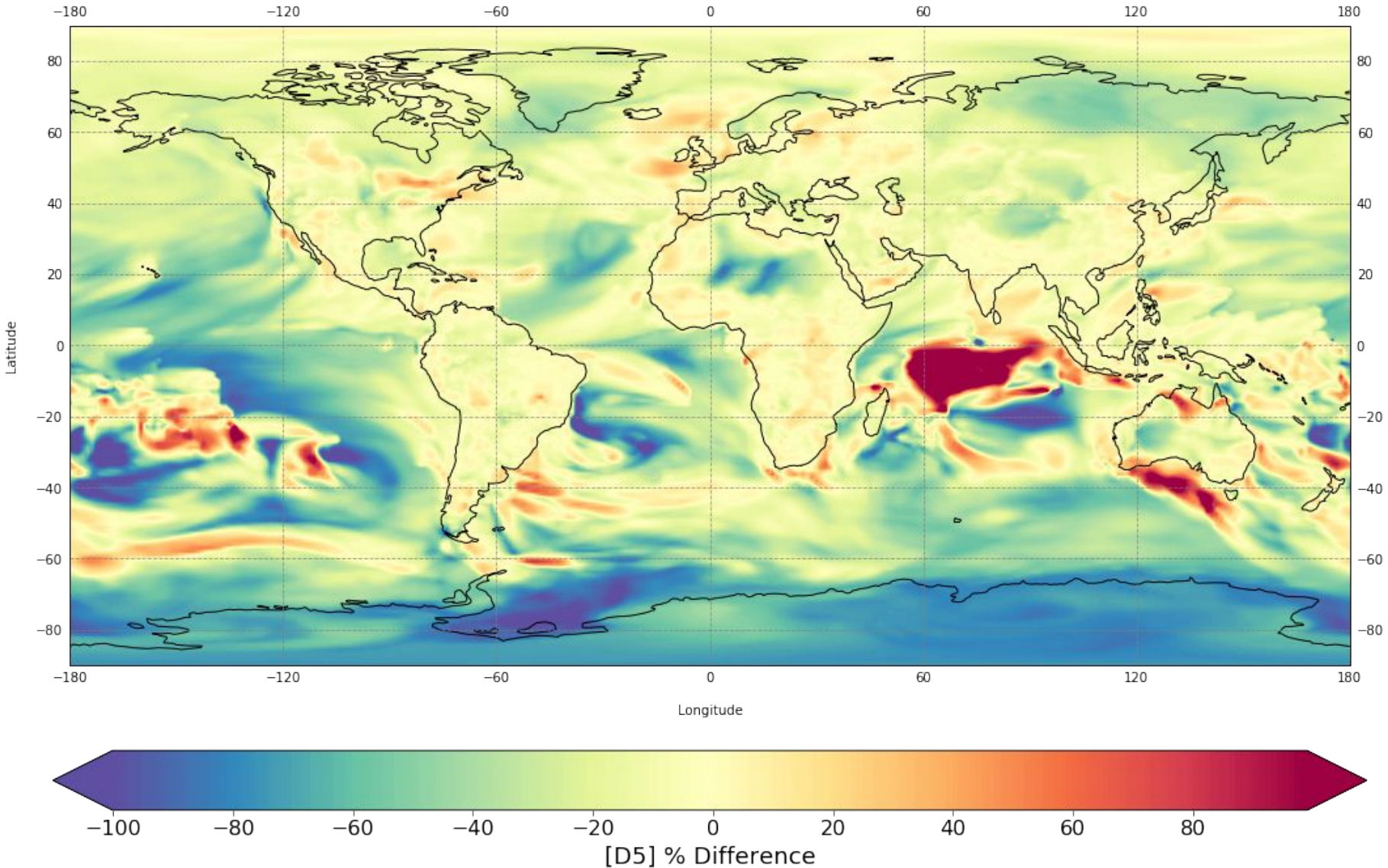
1. Have sufficient time to undergo significant oxidation and
2. Pass through a region with a large temperature deviation from 298k...
3. Which is highly oxidizing.



This may explain trends observed in model comparison for February such the larger percent increase in the Antarctic compared to Arctic and the large decrease in concentrations over the Indian Ocean.

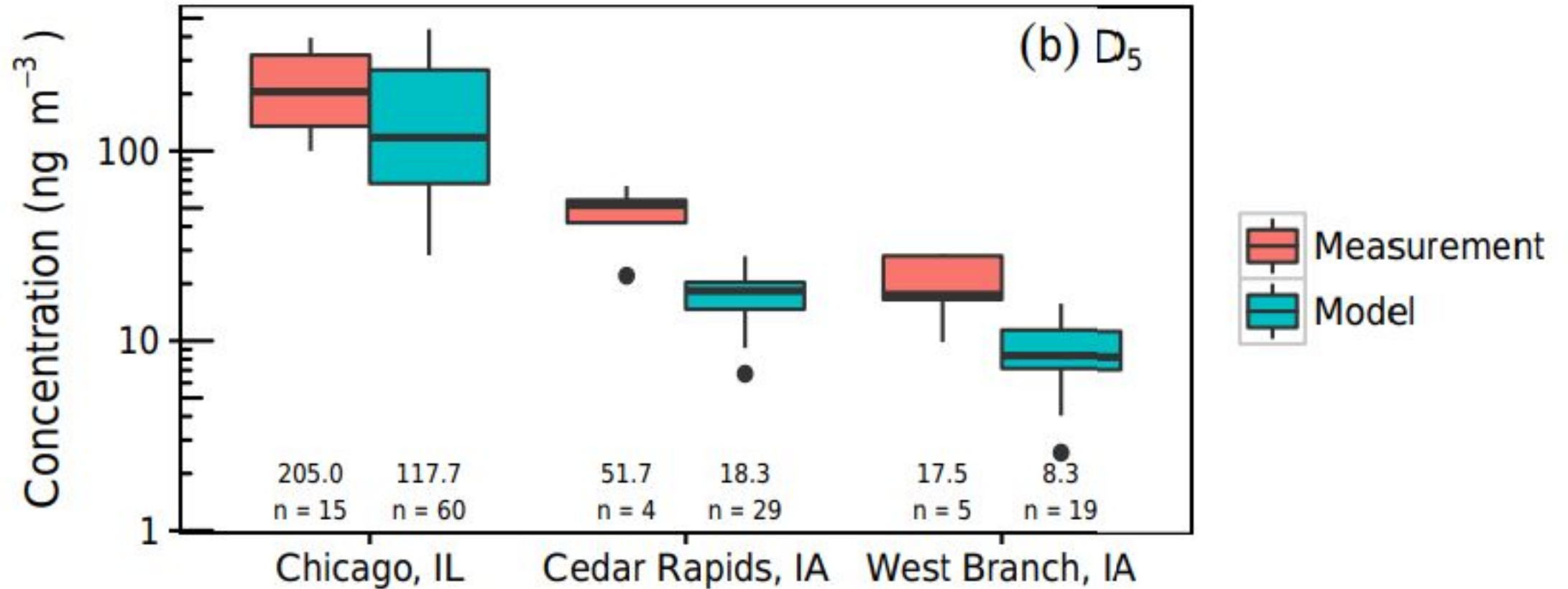


It also suggests that the regions most effected by temperature dependence likely vary throughout different parts of the year as oxidation and temperature conditions change.

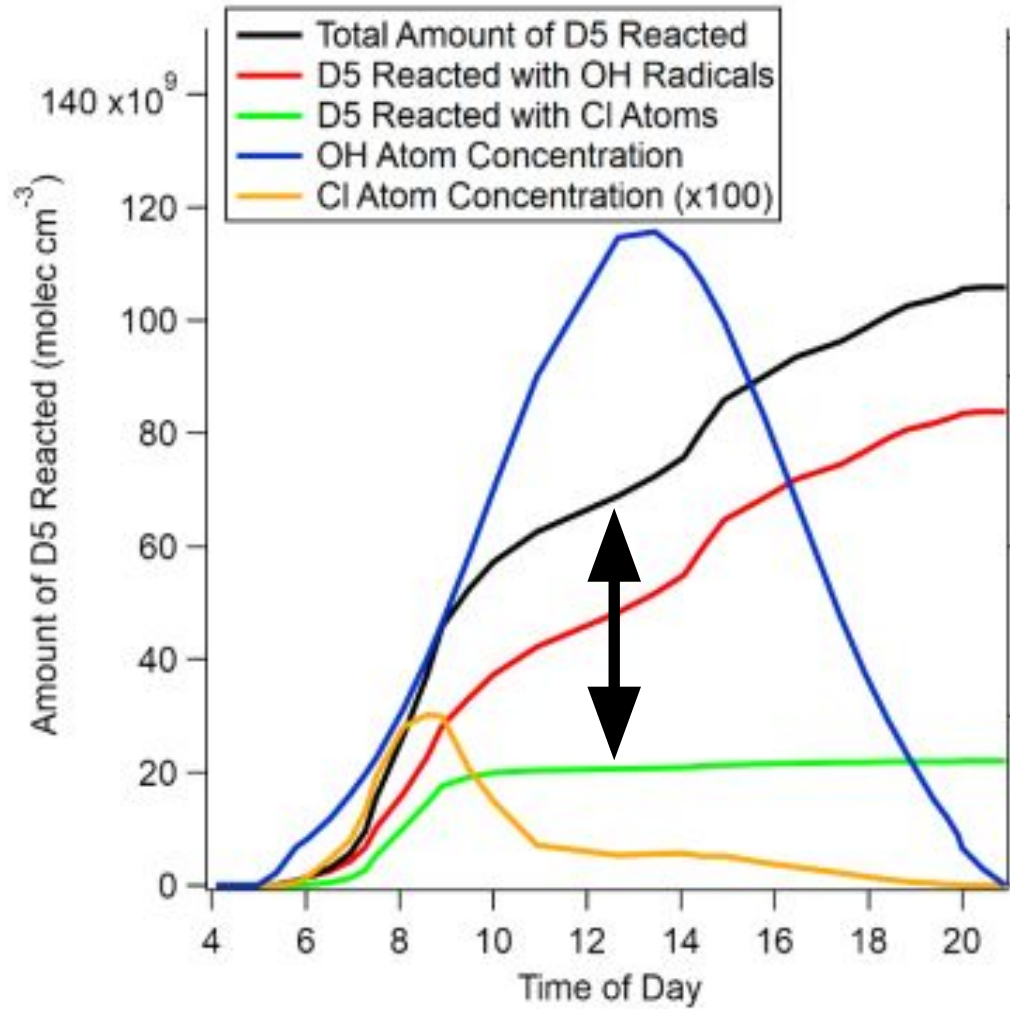


Creation of VMS Emissions Files

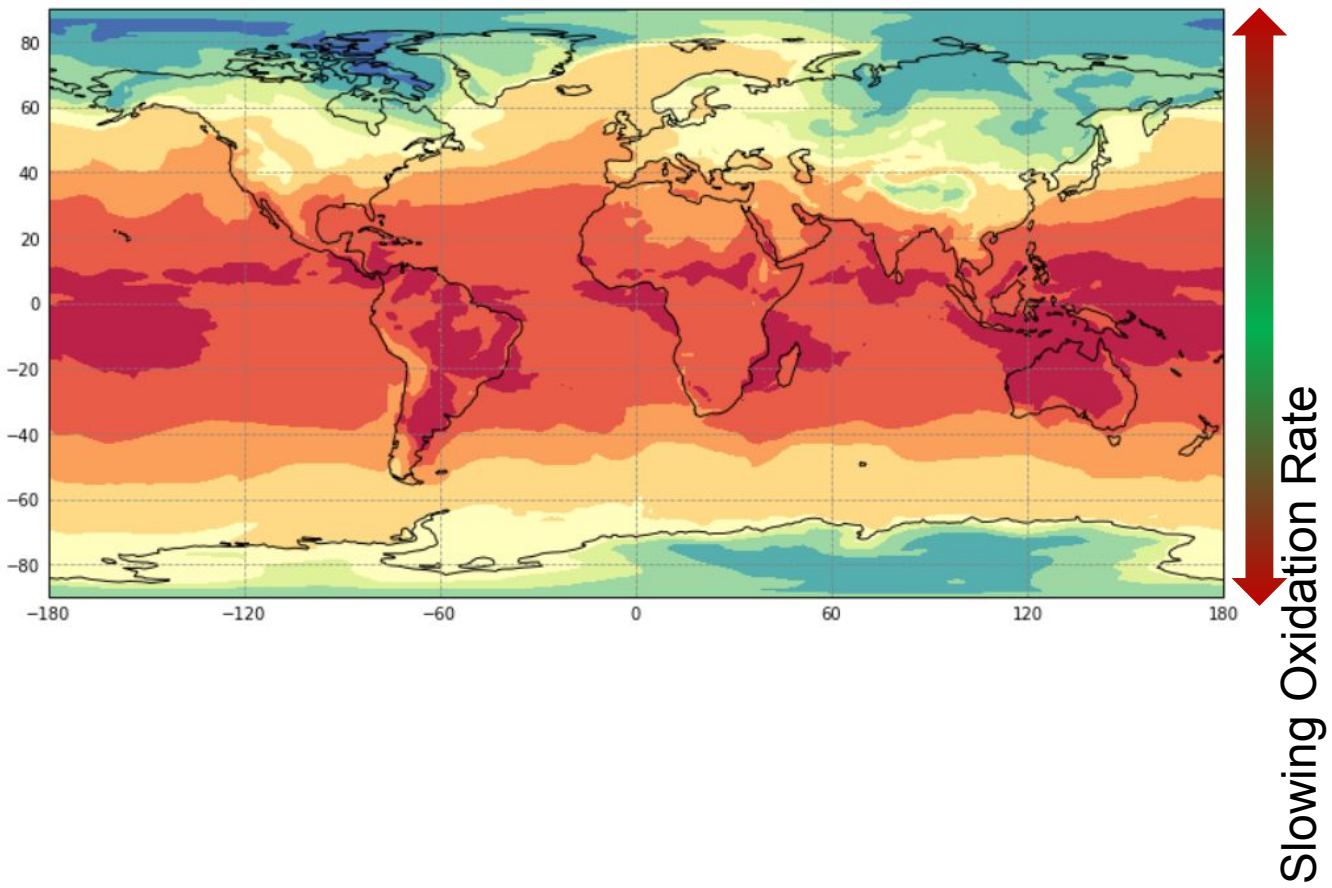
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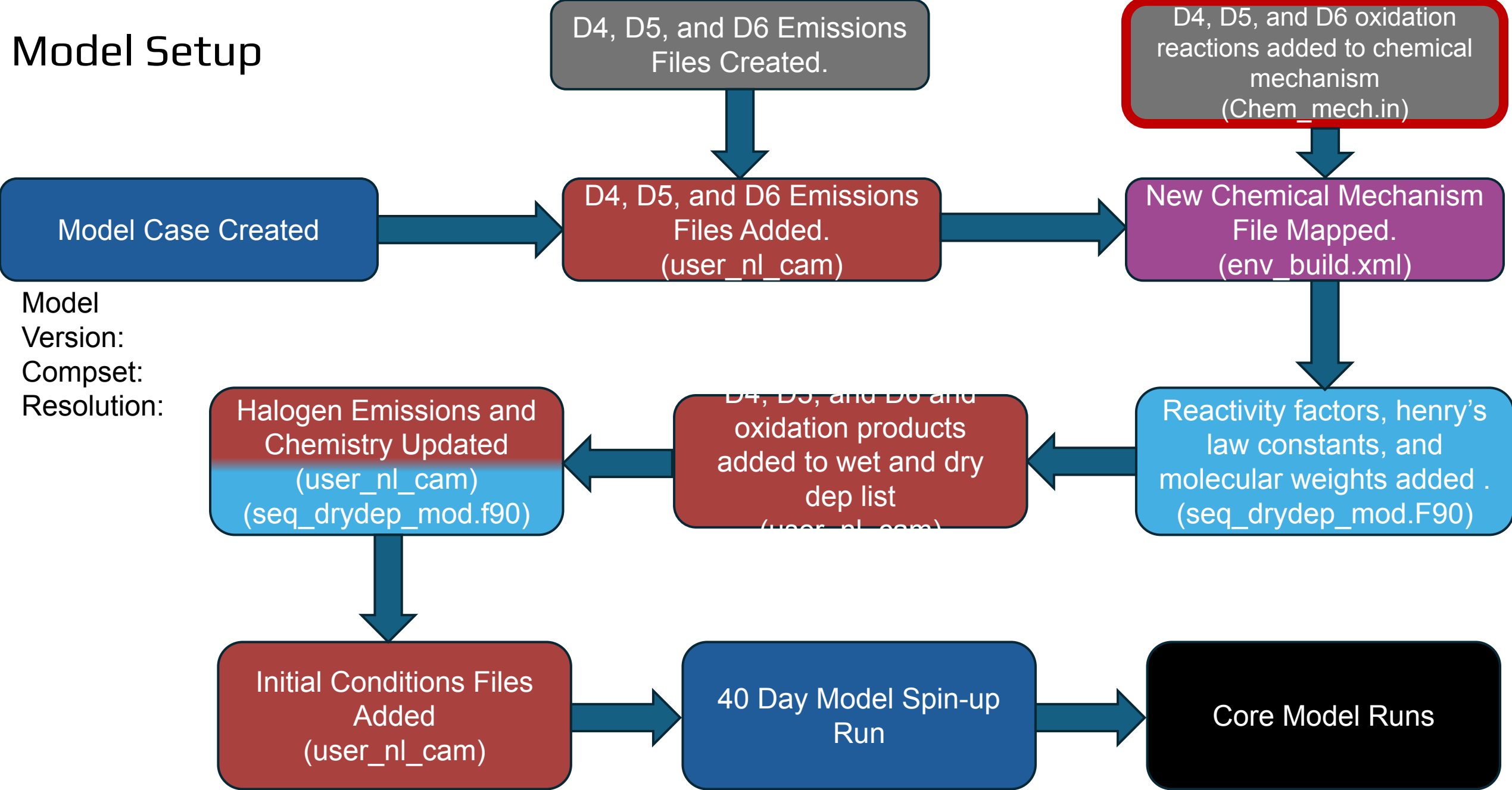
Why do we care about chlorine and temperature dependence?



Alton and Browne.
2020



Model Setup



Modification of the Chemical Mechanism

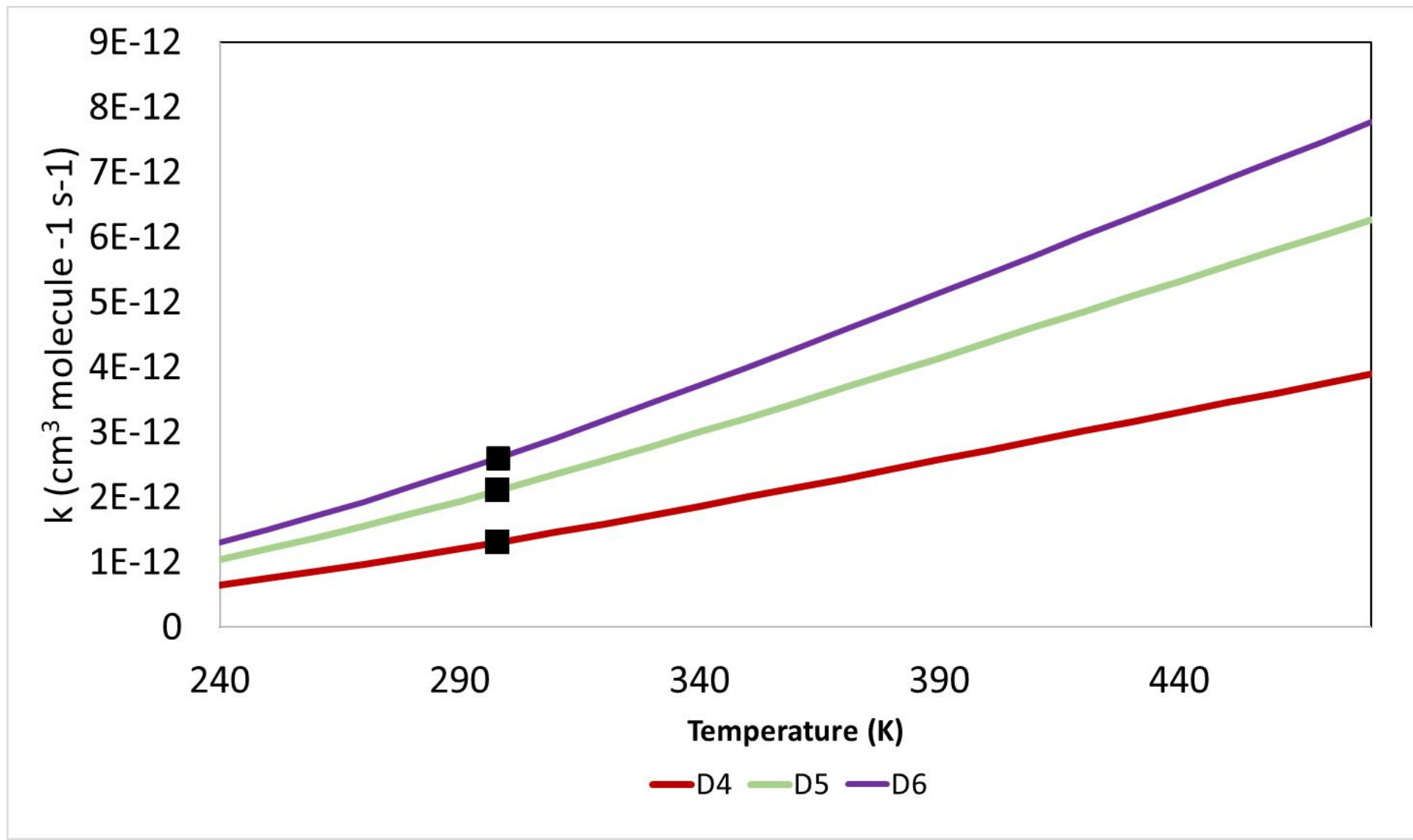
Estimates of the temperature dependence of VMS oxidation are limited and do not include the full range of VMS species. For this study, we chose to select data from Bernard et al. 2018 and use the most extreme estimate of the Arrhenius exponential term for all compounds in order to capture the greatest possible effect of temperature on the reaction rates.

$$k(T) = A * e^{\left(\frac{-Ea}{T}\right)}$$

Siloxane	A	E	Source
L2	1.87E-11	-791	Bernard et al. 2018
L3	1.96E-13	-657	Bernard et al. 2018
D3	1.29E-11	805	Bernard et al. 2018
D4	1.80E-11	816	Bernard et al. 2018
D4	1.1E-11	517	Safron et al. 2015
D5	1.5E-11	517	Safron et al. 2015
D6	1.7E-11	517	Safron et al. 2015
D3	1.31E-14	-1510	Xiao et al. 2015
D4	1.73E-12	-90	Xiao et al. 2015
D5	9.46E-12	410	Xiao et al. 2015

Modification of the Chemical Mechanism

Using this exponential term, the Arrhenius pre-exponential constant was set to a value so that at 298k the temperature dependent and non-temperature dependent rate constants for each compound were equal.



Modification of the Chemical Mechanism

Chem_mech.in was modified to include D4, D5, and D6 oxidation including both the temperature dependent OH reaction and chlorine oxidation.

```
*****
D5 -> C10H3005Si5,
D4 -> C8H2404Si4,
D6 -> C12H3506Si6,
oD5 -> C9H2806Si5,
oD6 -> C11H3307Si6,
oD4 -> C7H2205Si4
*** Siloxanes
*****
[D4o]          D4 + OH -> oD4          ; 2.33E-11, -859
[D5o]          D5 + OH -> oD5          ; 3.75E-11, -859
[D6o]          D6 + OH -> oD6          ; 4.65E-11, -859
[D4cl]         D4 + CL -> oD4          ; 1.20e-10
[D5cl]         D5 + CL -> oD5          ; 1.80e-10
[D6cl]         D6 + CL -> oD6          ; 2.60e-10
```

- Siloxane reactions do not interact with the rest of the model chemistry except for the consumption of hydroxyl and chlorine radicals.
- Oxidized products are only removed by wet and dry deposition so that they represent the concentration of all bulk oxidized products.