Universität Bremen

Stratospheric Chemistry Kinetics modeling

Practical Environmental Measurements Techniques

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Laboratory for Modeling and Observation of the Earth System

Stratospheric Chemistry

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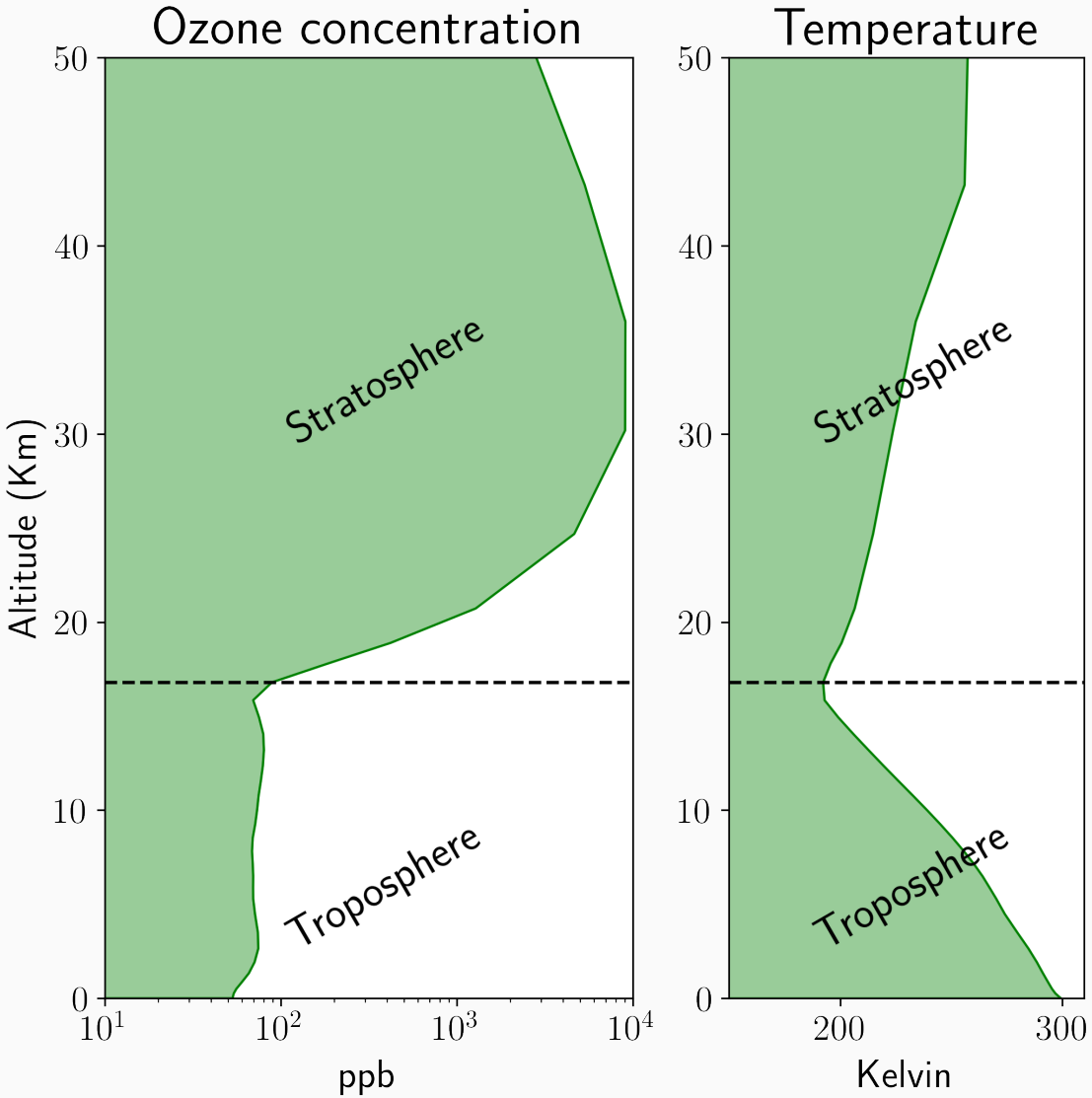
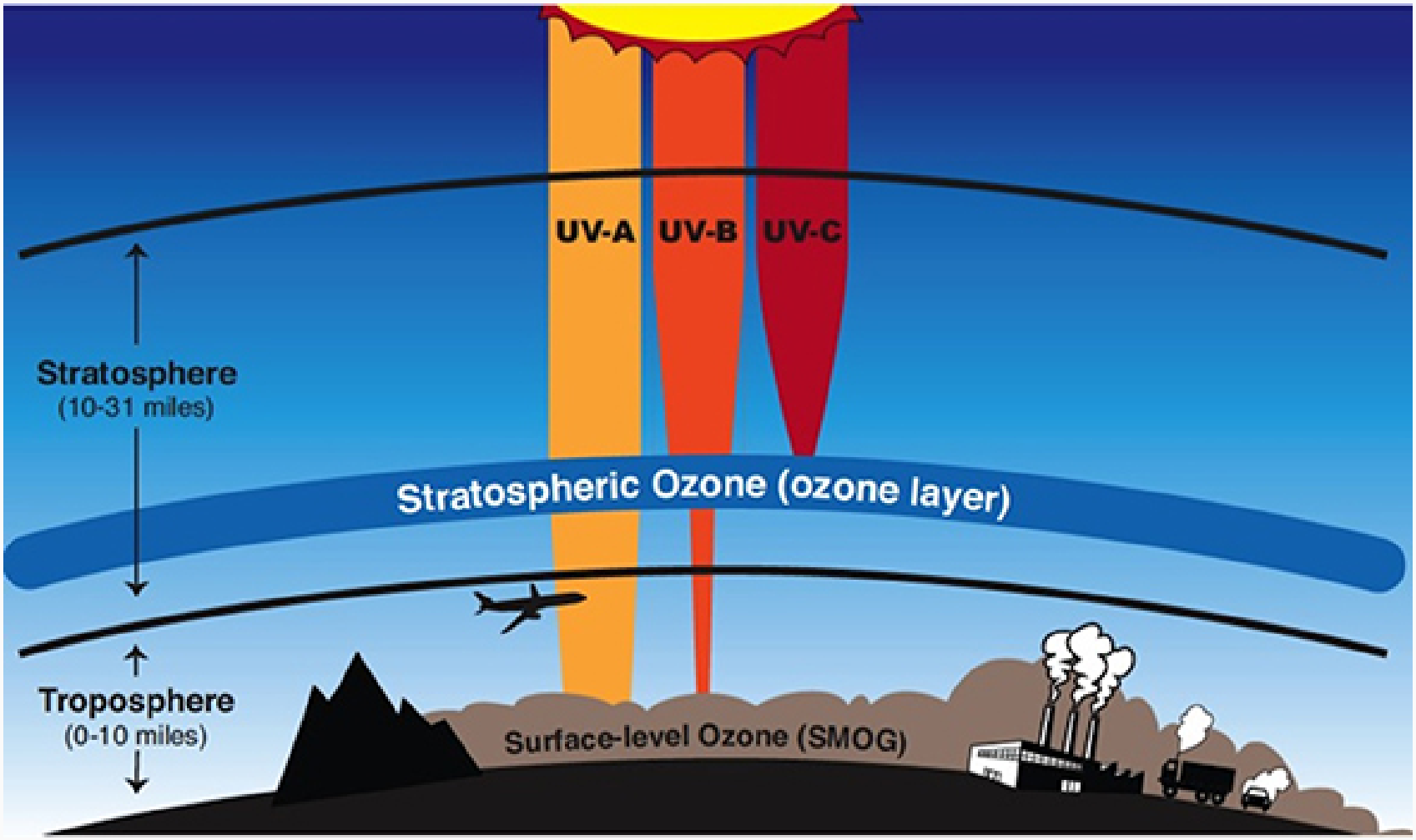
O_3 and temperature vertical distribution in the atmosphere



Produced using data from the TM4-ECPL model

Importance of the O_3 layer



Credit: NASA

Chapman mechanism

- Chapman theory
  - describes how sunlight converts the various forms of oxygen from one to another.
  - Explains why the highest content of ozone occurs in the layer between 15–50 km.
- Explains the stratospheric ozone layer!
- Fails to quantitatively explain the ozone concentrations in the stratosphere.

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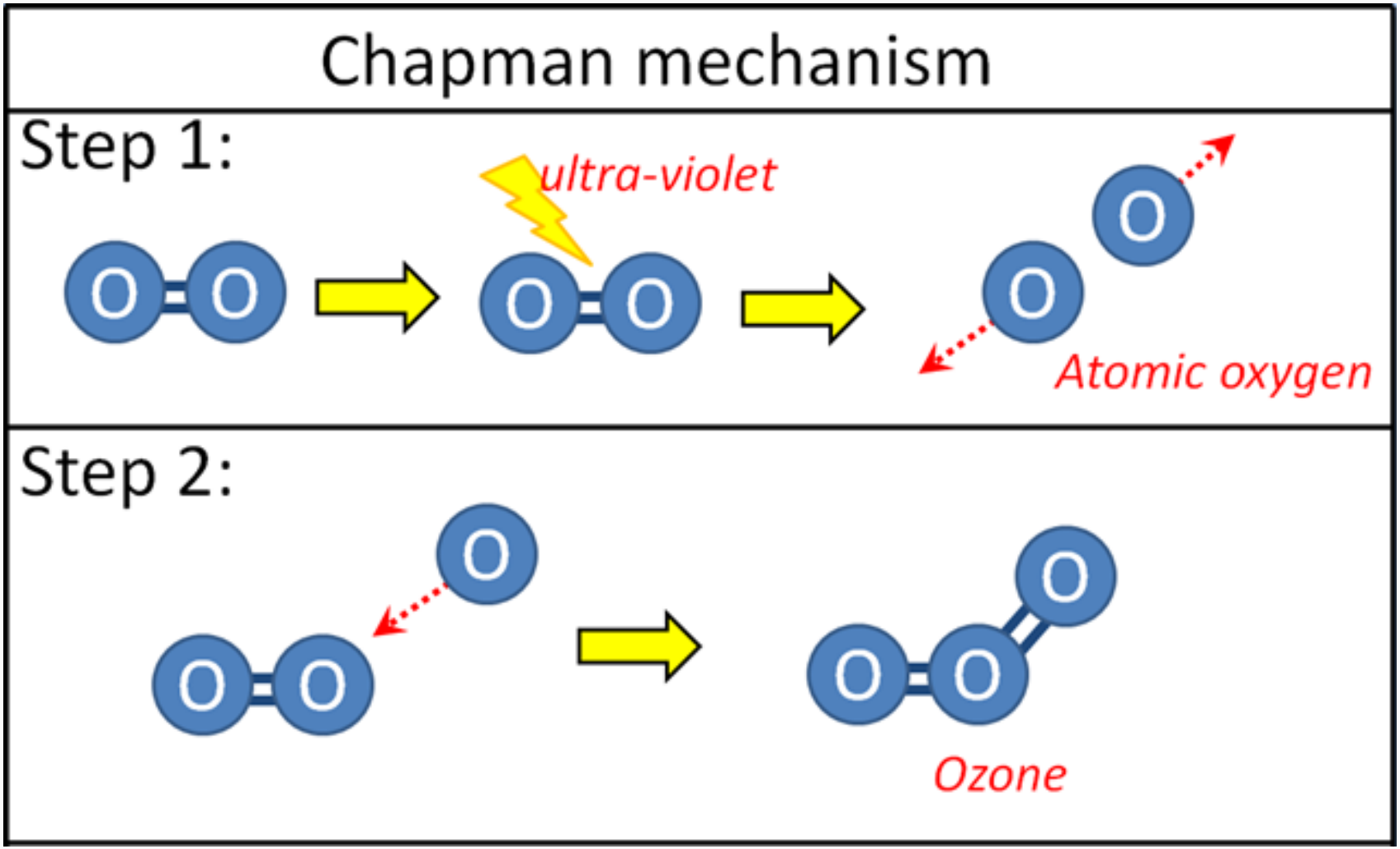
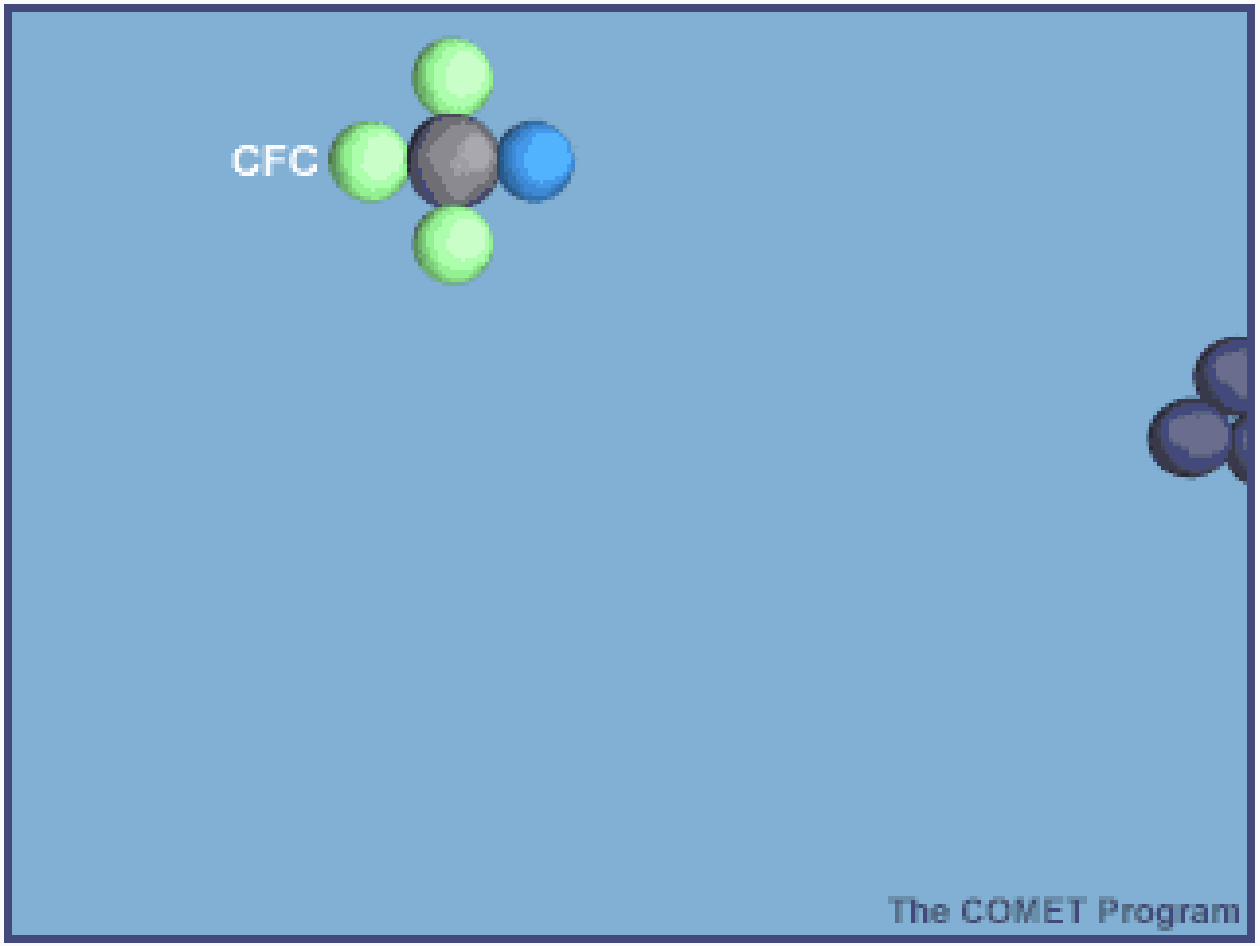
Chapman cycle



Source: Connolly and Connolly, 2013

Catalytic ozone destruction by CFCs



Credit:UCAR/COMET

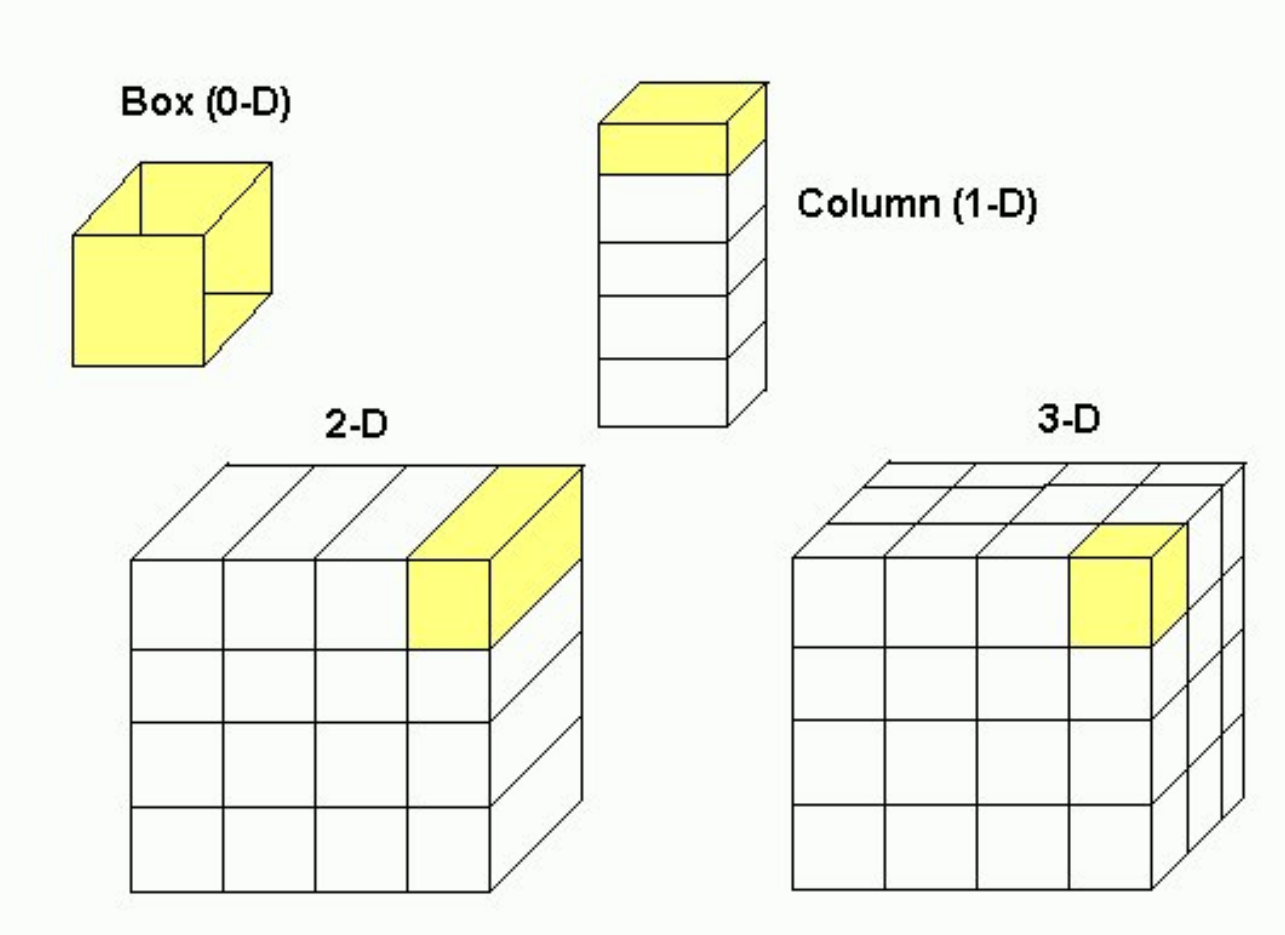
Atmospheric Models

What is a model?

Atmospheric Model

A **tool** based on **mathematics** aimed to give a *numerical representation* of our **current knowledge** of the processes determining atmospheric composition.

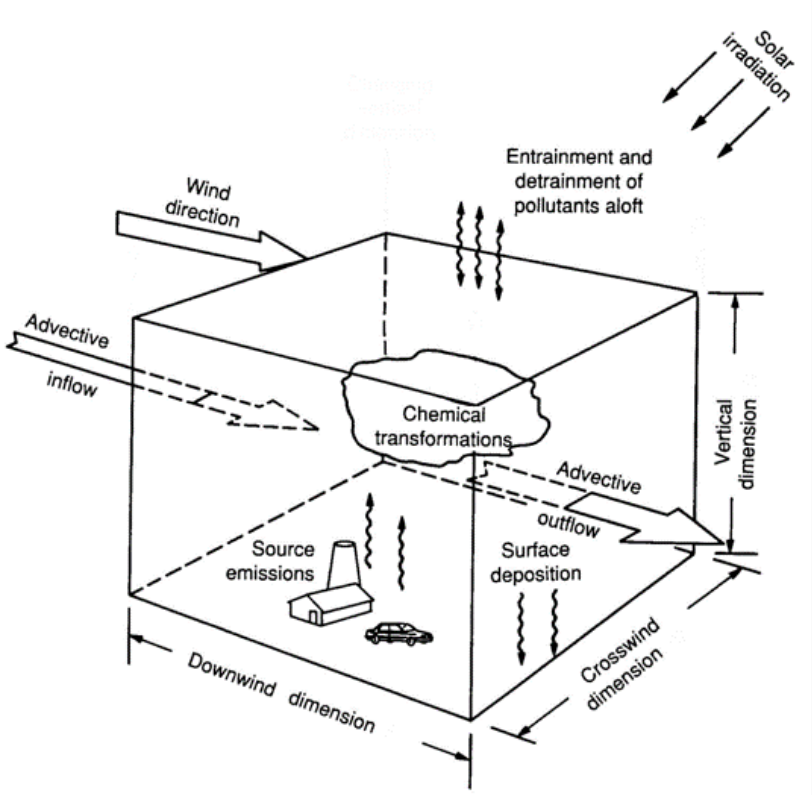
Model dimensions



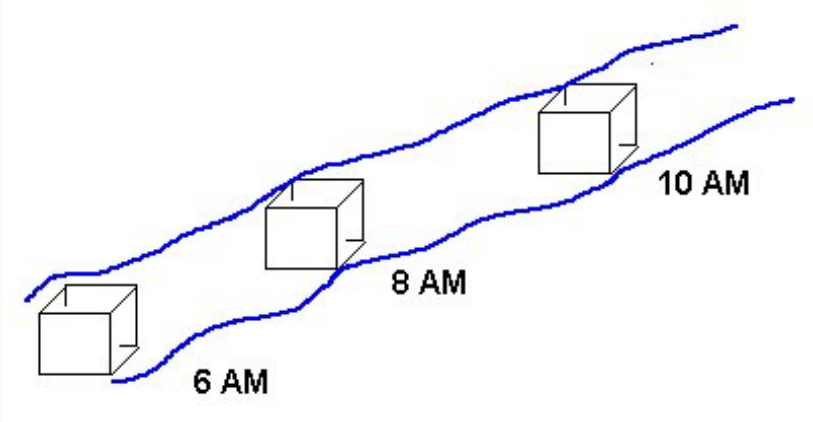
http://irina.eas.gatech.edu/lectures/Lec29.htm

Box (or 0D) models

Eulerian



Lagrangian



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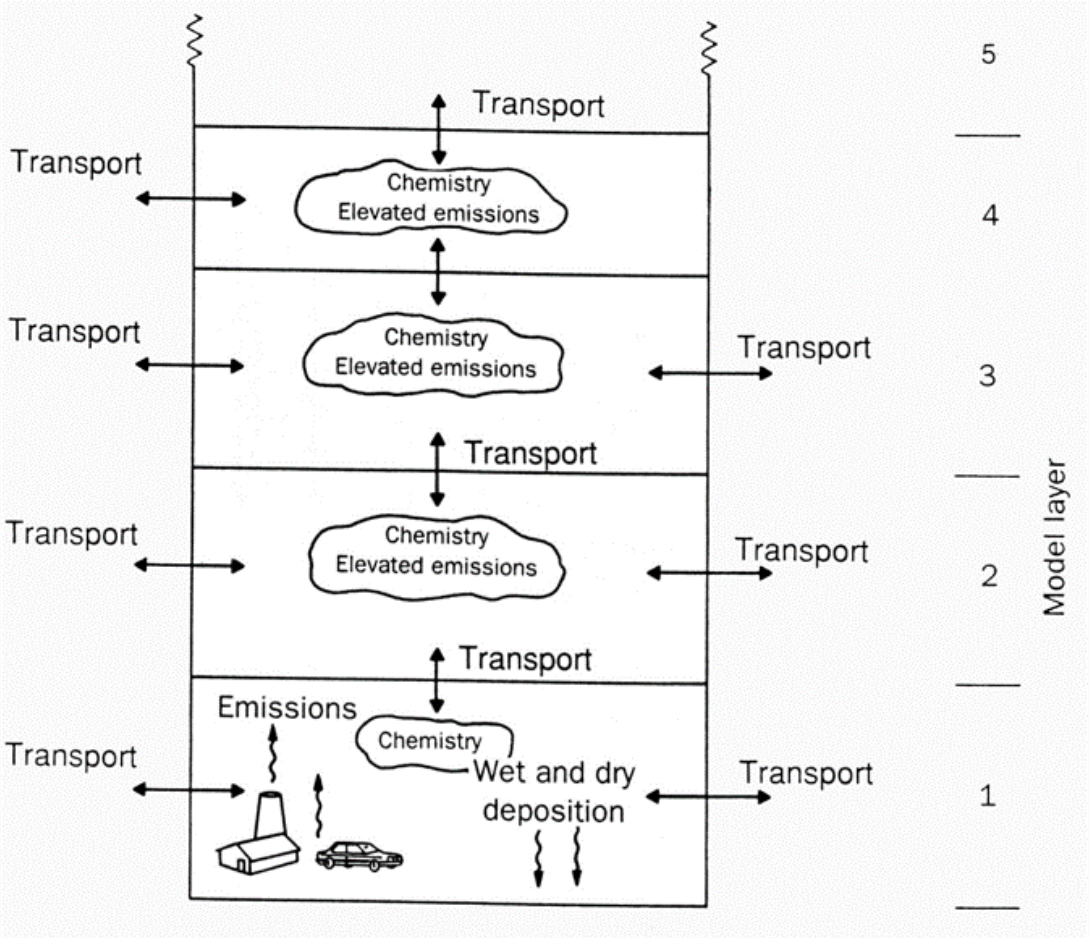
Single column (or 1D) models



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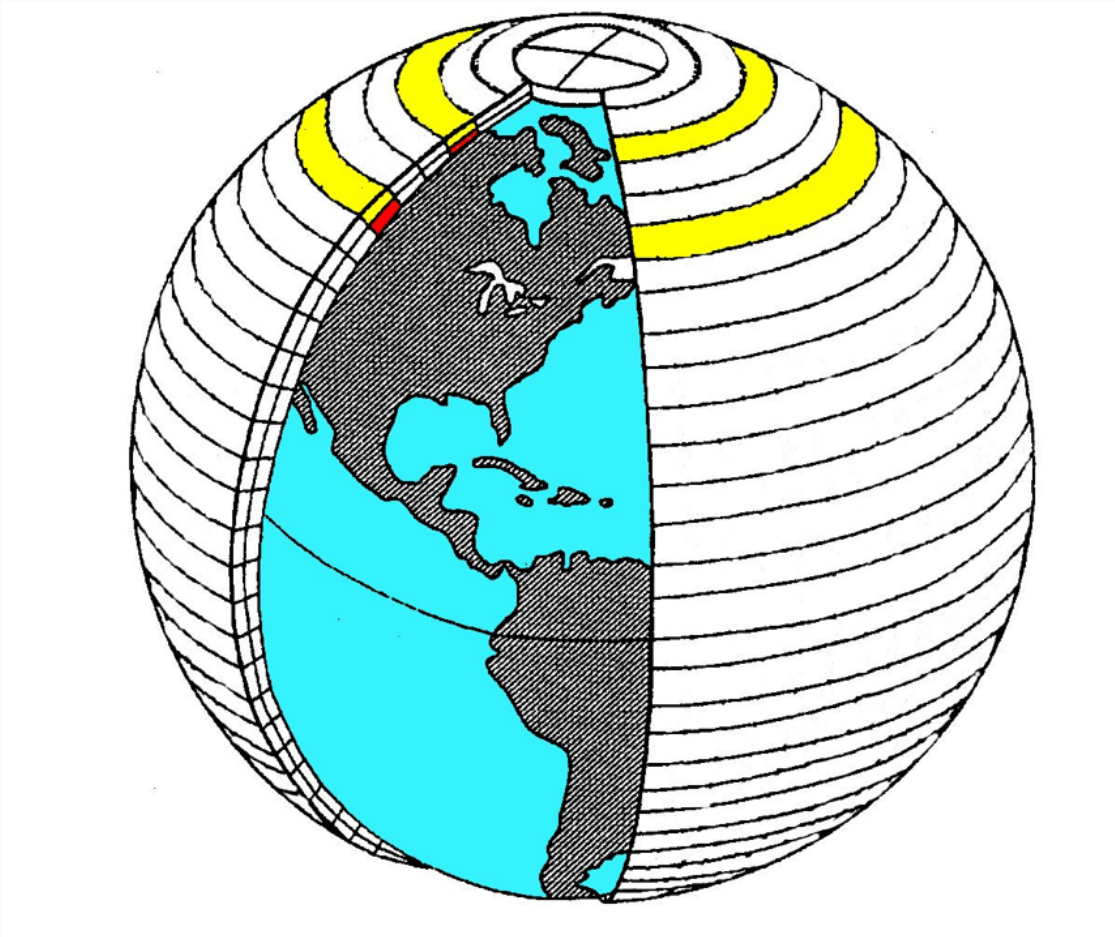
2D models



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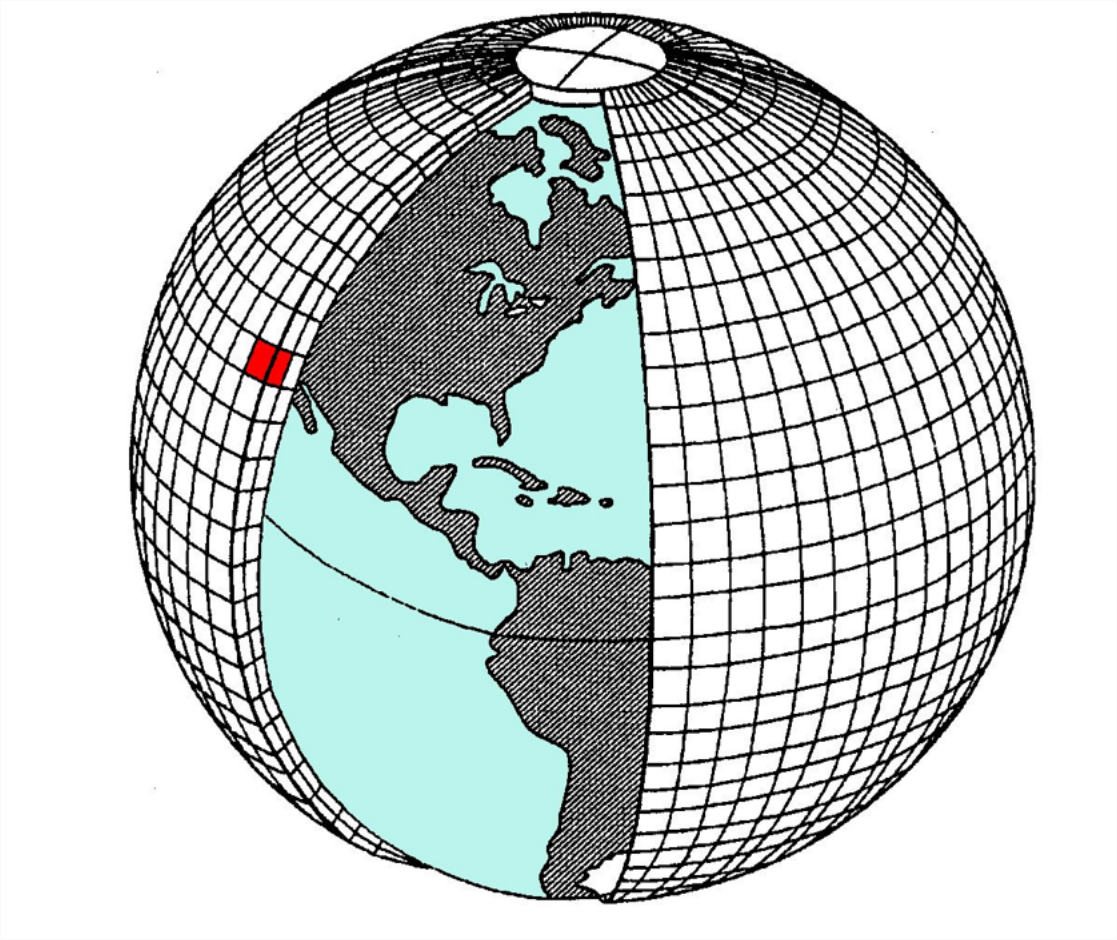
3D models



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KPP, Kinetic PreProcessor

What is KPP?

KPP – Kinetic PreProcessor

The KPP kinetic preprocessor is a software tool that assists the computer simulation of chemical kinetic systems. The concentrations of a chemical system evolve in time according to the differential law of mass action kinetics. A numerical simulation requires an implementation of the differential laws and a numerical integration in time.

What does this mean?

- KPP is NOT a model!
- KPP produces a model
- based on human readable chemical equations and reaction rates.
- The produced model can solve the chemical equilibrium system's evolution over time

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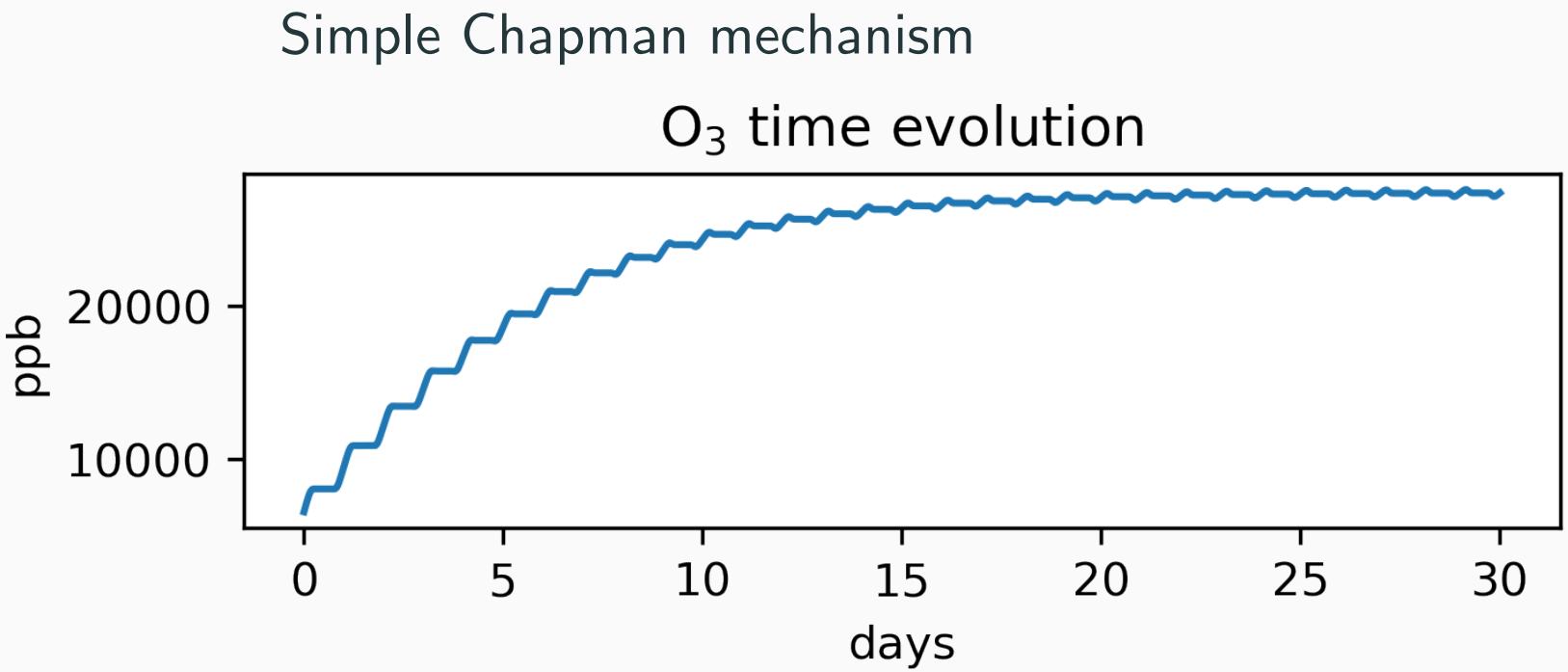
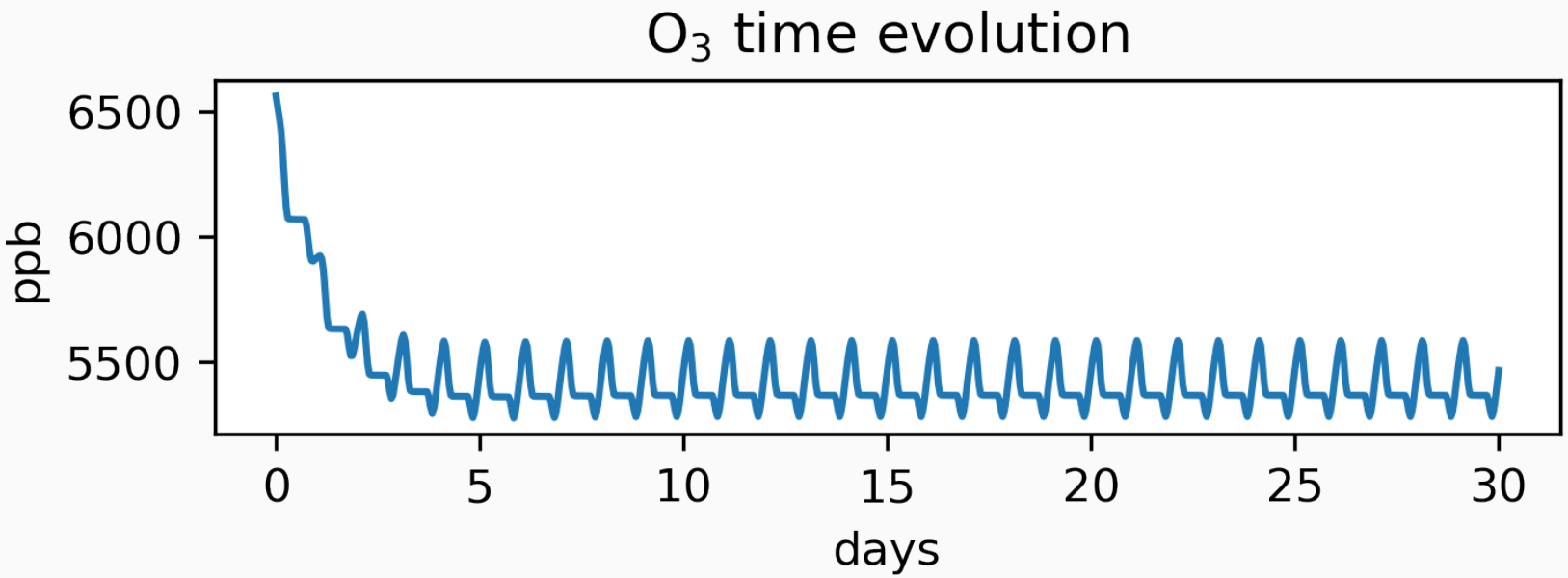
Ozone concentrations as simulated by a KPP produced model



Ozone concentrations as simulated by a KPP produced model

Full stratospheric chemistry mechanism containing more than 100 reactions



Example

Creating a KPP model

- Know the chemical equations and reaction rates!
- Create the mandatory KPP files
  - model.kpp ← This defines the model
  - model.eqn ← This contains all the chemical equations and reaction rate coefficients
  - model.spc ← This defines all the different chemical species that are present in the model
  - model.def ← This defines integration time, integrator, etc.
- Create the model
- Compile and run the model
- Process the results

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The smog.kpp file

```
#MODEL       smog
#LANGUAGE    Fortran90
#INTEGRATOR rosenbrock
#DRIVER      general
```

The smog.eqn file

```
#EQUATIONS

{ A Photochemical Smog Reaction Mechanism }

{ 1.}  NO2 + hv = NO + O :                    0.533 ;
{ 2.}  O + O2 = O3       :                 2.183E-5 ;
{ 3.}  NO + O3 = NO2 + O2 :                    26.59 ;
{ 4.}  RH + OH = RO2 + H2O :                3.775E+3 ;
{ 5.}  RCHO + OH = RCOO2 + H2O :            2.341E+4 ;
{ 6.}  RCHO + hv = RO2 + HO2 + CO :          1.91E-4 ;
{ 7.}  HO2 + NO = NO2 + OH :                1.214E+4 ;
{ 8.}  RO2 + NO = NO2 + RCHO + HO2 :        1.127E+4 ;
{ 9.}  RCOO2 + NO = NO2 + RO2 + CO2 :       1.127E+4 ;
{10.}  OH + NO2 = HNO3 :                    1.613E+4 ;
{11.}  RCOO2 + NO2 = RCOO2NO2 :             6.893E+3 ;
{12.}  RCOO2NO2 = RCOO2 + NO2 :             2.143E-2 ;
```

The smog.spc file

```
#include atoms

 #DEFVAR
    O           = O ;           {oxygen atomic ground state (3P)}
    O3          = 3O ;          {ozone}
    NO          = N + O ;       {nitric oxide}
    NO2         = N + 2O ;      {nitrogen dioxide}
    NO3         = N + 3O ;      {nitrogen trioxide}
    N2O5        = 2N + 5O ;     {dinitrogen pentoxide}
    HNO3        = H + N + 3O ;  { nitric acid }
    HNO4        = H + N + 4O ;  {HO2NO2 pernitric acid}
    H           = H ;           {hydrogen atomic ground state (2S)}
    OH          = O + H ;       {hydroxyl radical}
    HO2         = H + 2O ;      {perhydroxyl radical}
    H2O2        = 2H + 2O ;     {hydrogen peroxide}
    CH3         = C + 3H ;      {methyl radical}
    CH3O        = C + 3H + O ;  {methoxy radical}
    CH3O2       = C + 3H + 2O ; {methylperoxy radical}
    CH3OOH      = C + 4H + 2O ; {CH4O2      methylperoxy alcohol}
    HCO         = H + C + O ;   {CHO  formyl radical}
    CH2O        = C + 2H + O ;  {formalydehyde}

    RH          = ignore ;
    RO2         = ignore ;
    RCHO        = ignore ;
    RCO2        = ignore ;
    RCO2NO2     = ignore ;
```

The smog.spc file

```
#DEFFIX
    H2O          = H + 2O ;       {water}
    H2           = 2H ;           {molecular hydrogen}
    O2           = 2O ;           {molecular oxygen}
    N2           = 2N ;           {molecular nitrogen}
    CH4          = C + 4H ;       {methane}
    CO           = C + O ;        {carbon monoxide}
    CO2          = C + 2O ;       {carbon dioxide}
```

The smog.def file

```
#include smog.spc
#include smog.eqn

#LOOKATALL
#MONITOR O3;

#INITVALUES

CFACTOR = 1.;
ALL_SPEC = 1.0E-8;
RH   = 2.0 ;
RCHO = 2.0 ;
NO   = 0.5 ;
NO2  = 0.1 ;
H2O  = 1.3E+4 ;
O2   = 2.0E+5 ;
```

The smog.def file

```
#INLINE F90_INIT
        TSTART = 0
        TEND = TSTART + 600
        DT = 60.0
        TEMP = 298
#ENDINLINE
```

Next steps

- Create the model using KPP

  ```
  kpp smog.kpp
  ```

- compile the model

  ```
  make -fMakefile_smog
  ```

- Run the newly created model

  ```
  ./smog.exe
  ```

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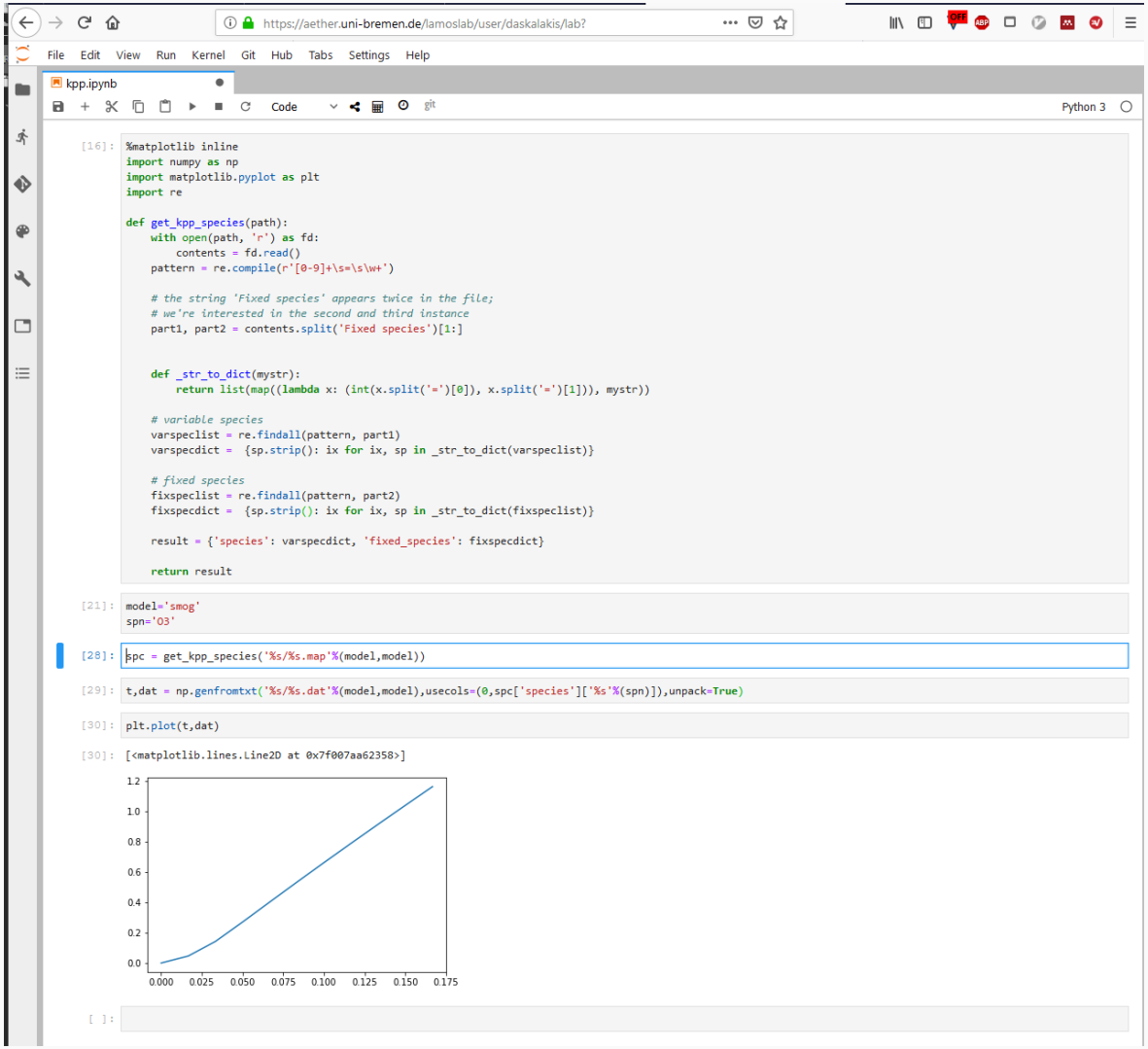
Result processing

If the run is successful, you can now start processing the results:



Thank you for your attention