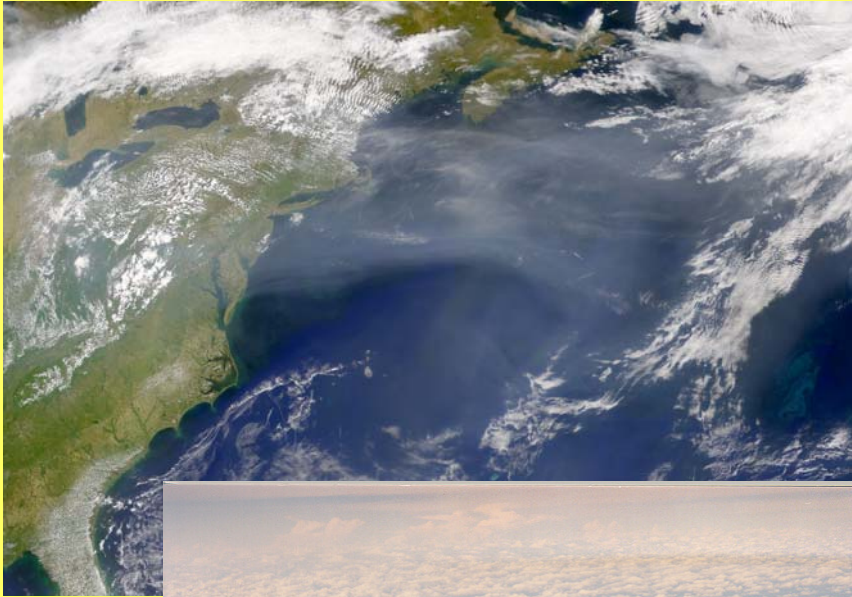


The Impact of Primary Marine Aerosol on Atmospheric Chemistry, Radiation, and Climate

A CCSM Development Study

Michael S. Long – Department of Environmental Sciences
University of Virginia

Role of aerosols in Atmospheric Chemistry & Climate



Role of aerosols in Atmospheric Chemistry & Climate

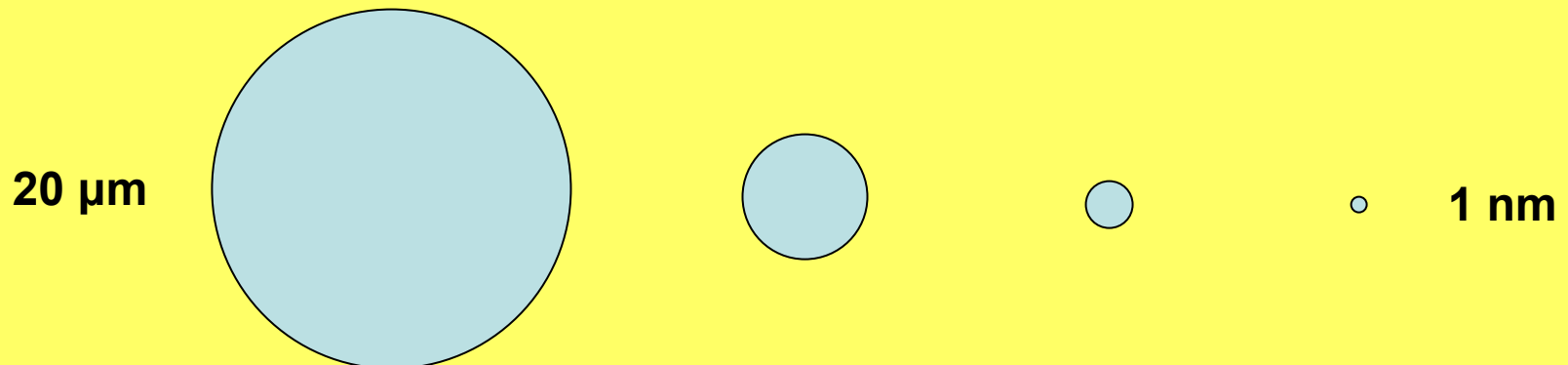
Marine Aerosols:

Surface ocean: sea-salt, OC

Secondary constituents: NO_3^- , SO_4^{2-} , OC, mineral dusts

Composition and abundance controls influence.

Size determines evolution and lifetime (*range: 1 nm to >20 μm*)

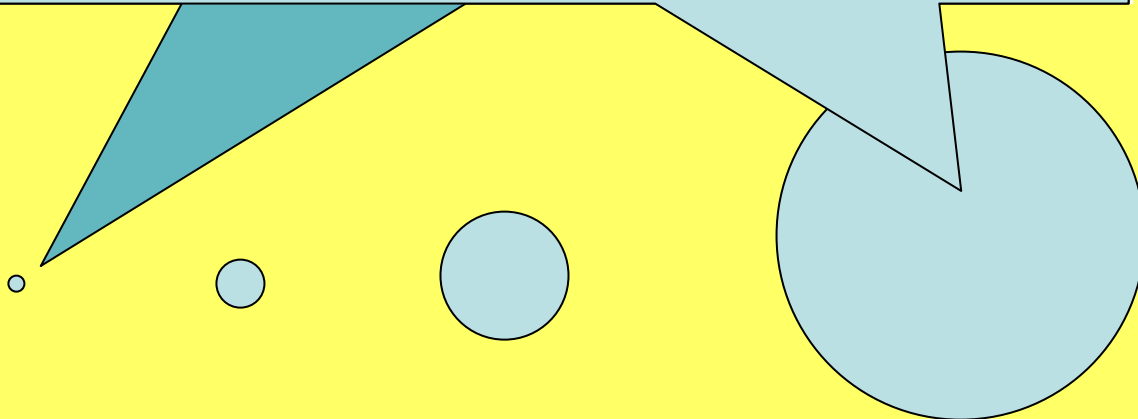


Role of aerosols in Atmospheric Chemistry & Climate

Larger Volume titrated more slowly by
acid gases.

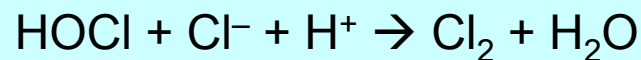
Capable of scavenging lots of acidity from the
atmosphere

Shorter lifetimes remove many gas-phase
constituents from the system

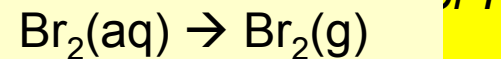
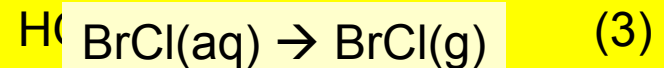
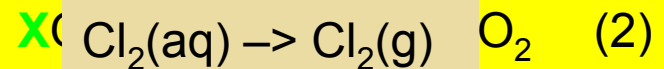
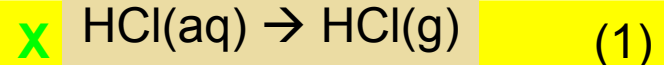
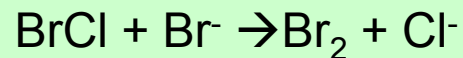
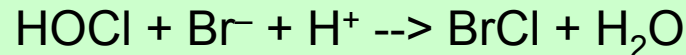
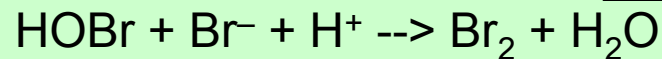


Role of aerosols in Atmospheric Chemistry & Climate

Chlorine Chemistry



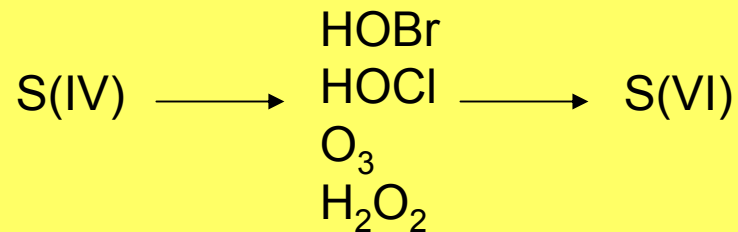
Bromine Chemistry



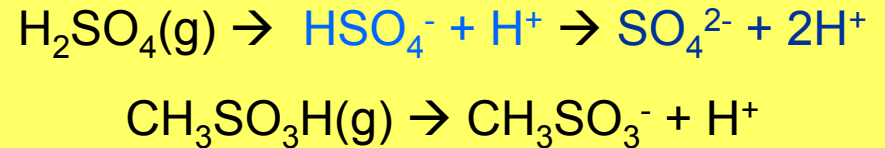
Role of aerosols in Atmospheric Chemistry & Climate

Sulfur Chemistry

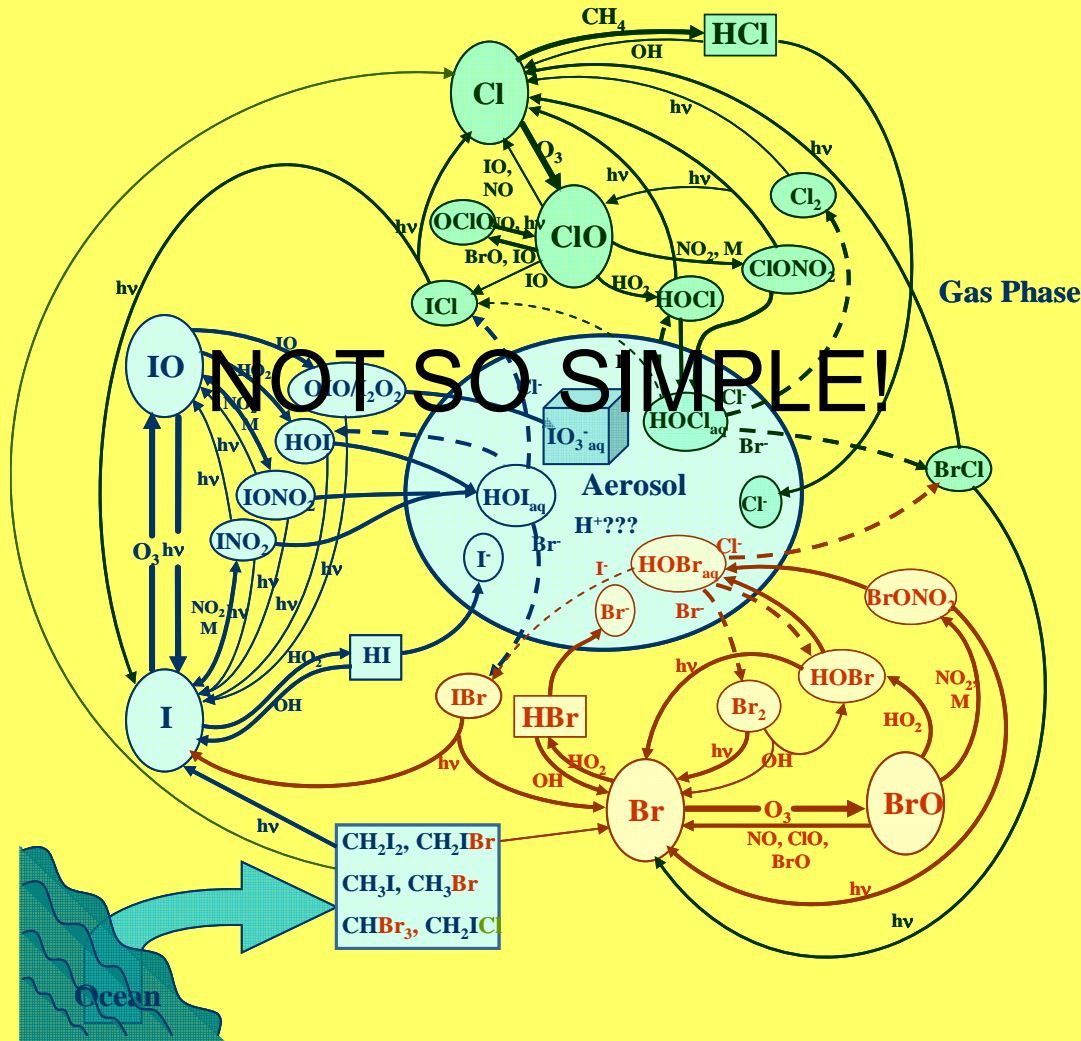
S(IV) Oxidation



S(VI) Uptake



Role of aerosols in Atmospheric Chemistry & Climate



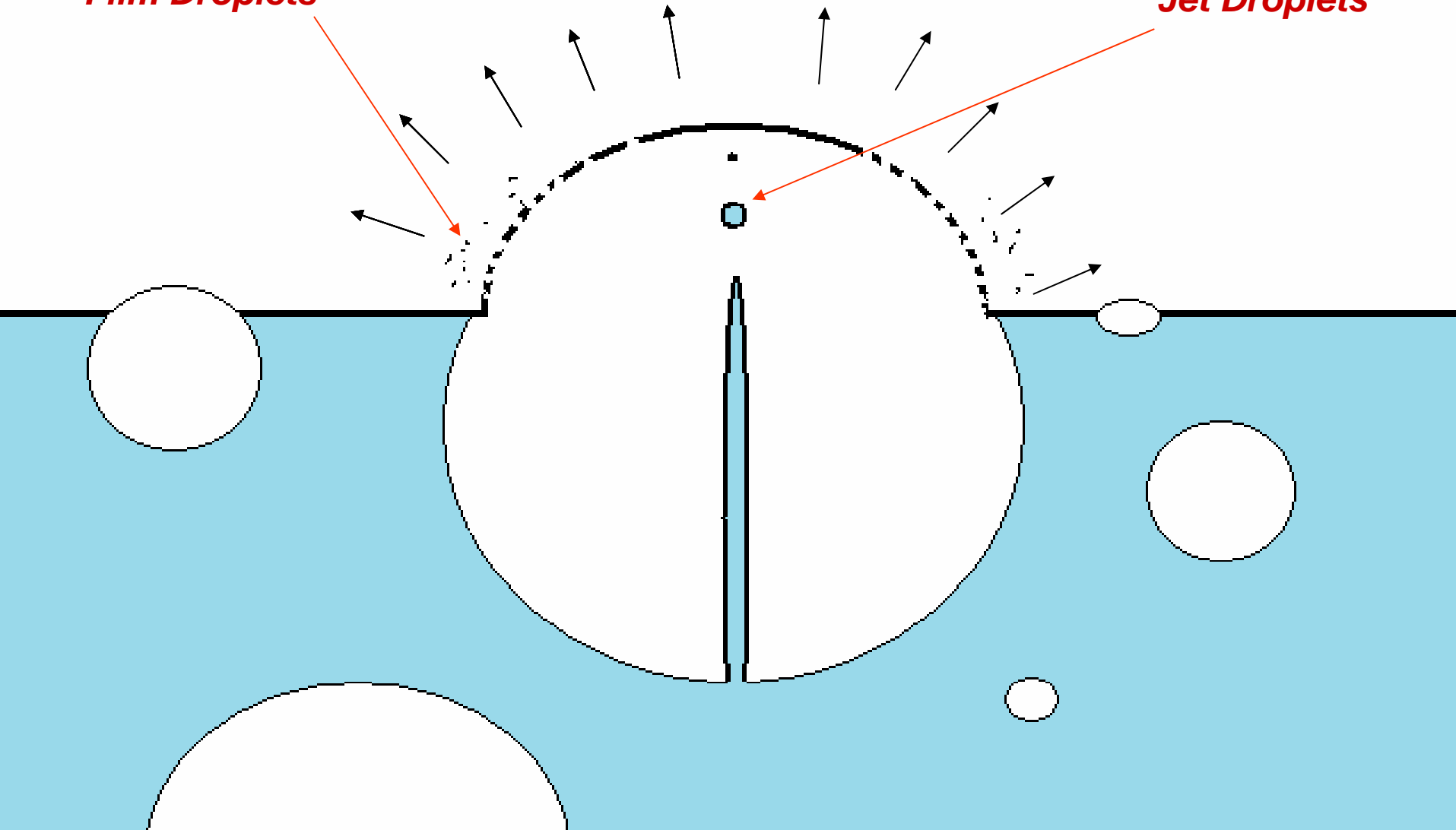
U_*



Bubble bursting

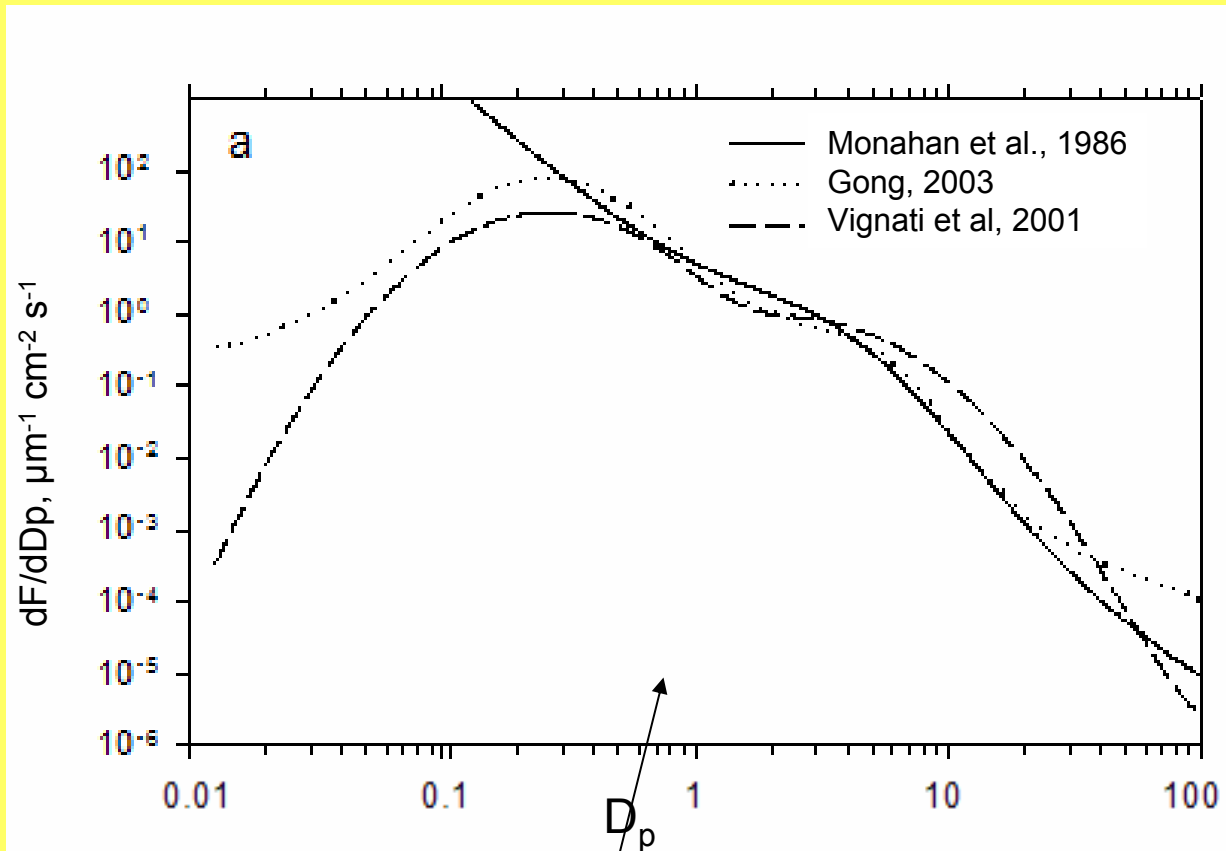
Film Droplets

Jet Droplets



U_*

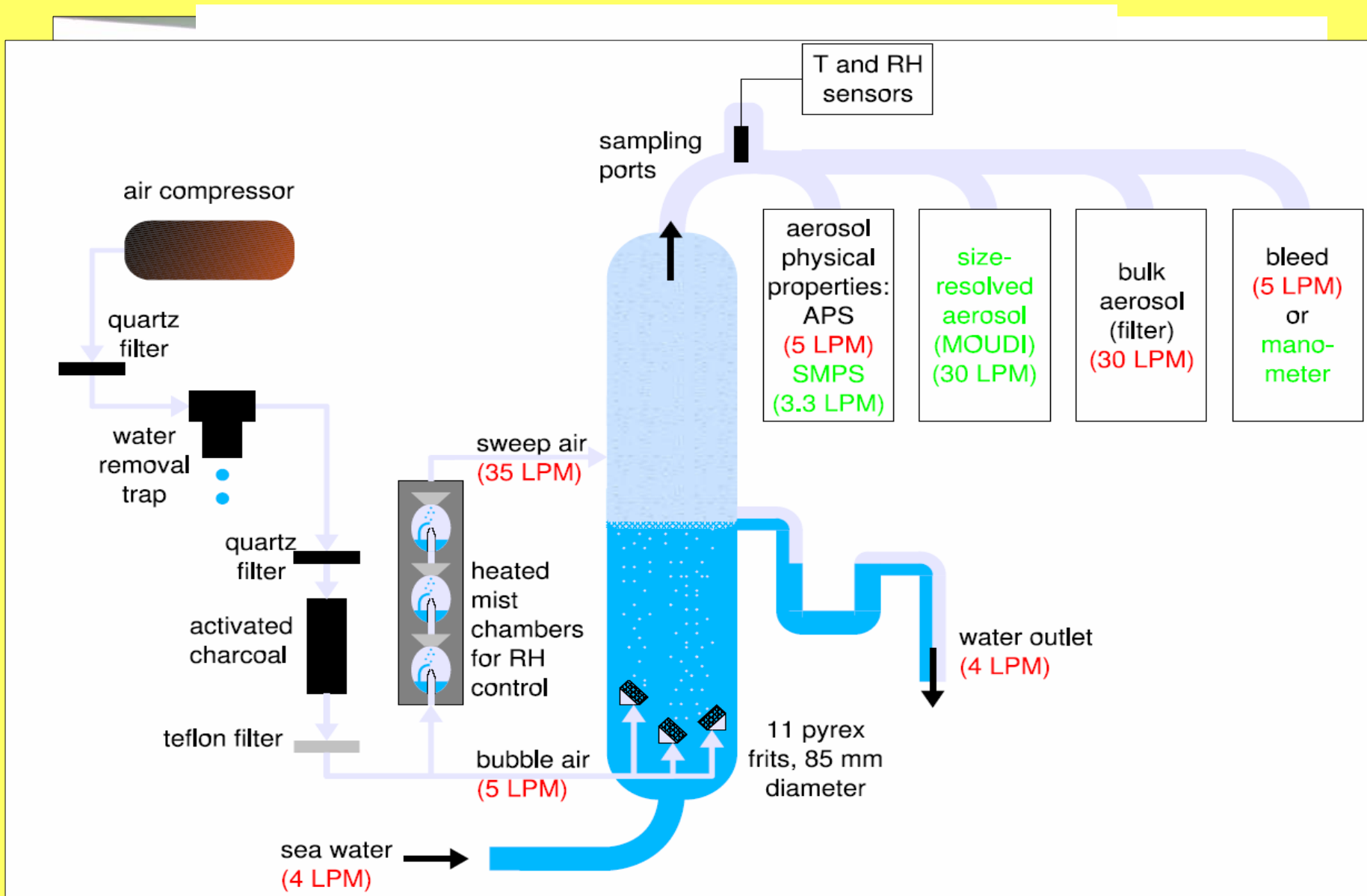




$$N(D_p) = F(D_p)_{up} - F(D_p)_{down}$$

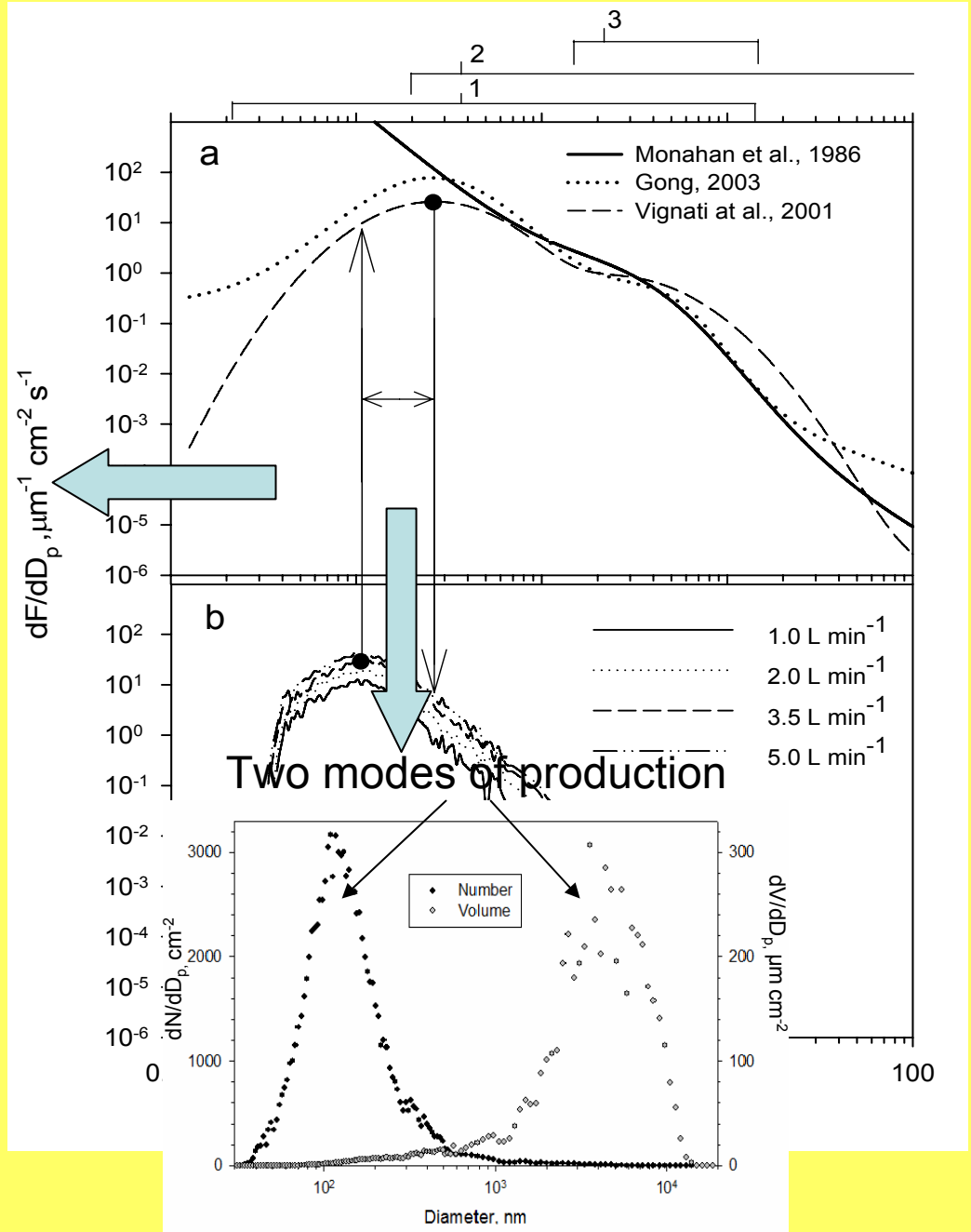
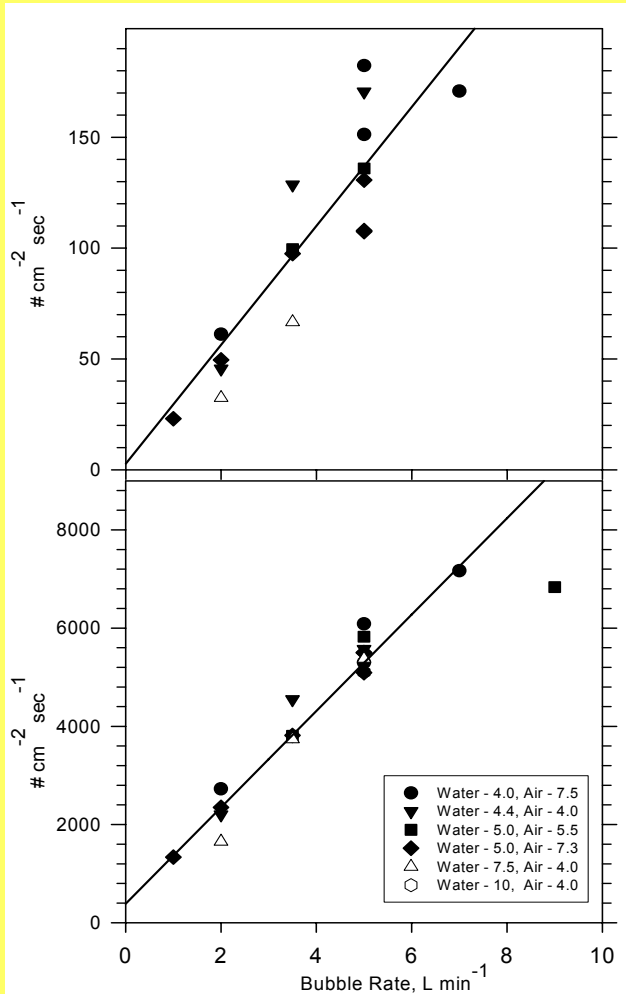
Measured

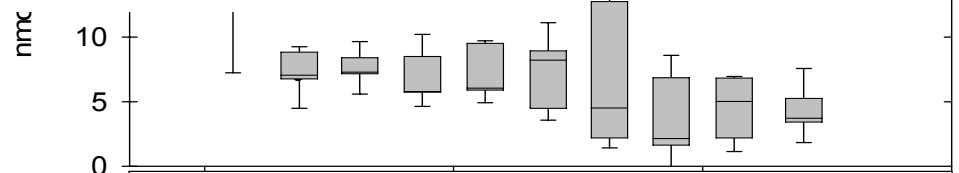
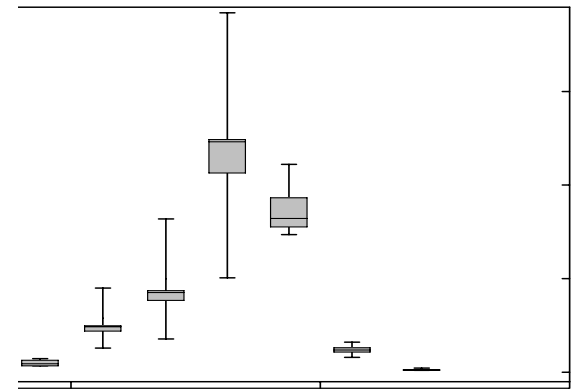
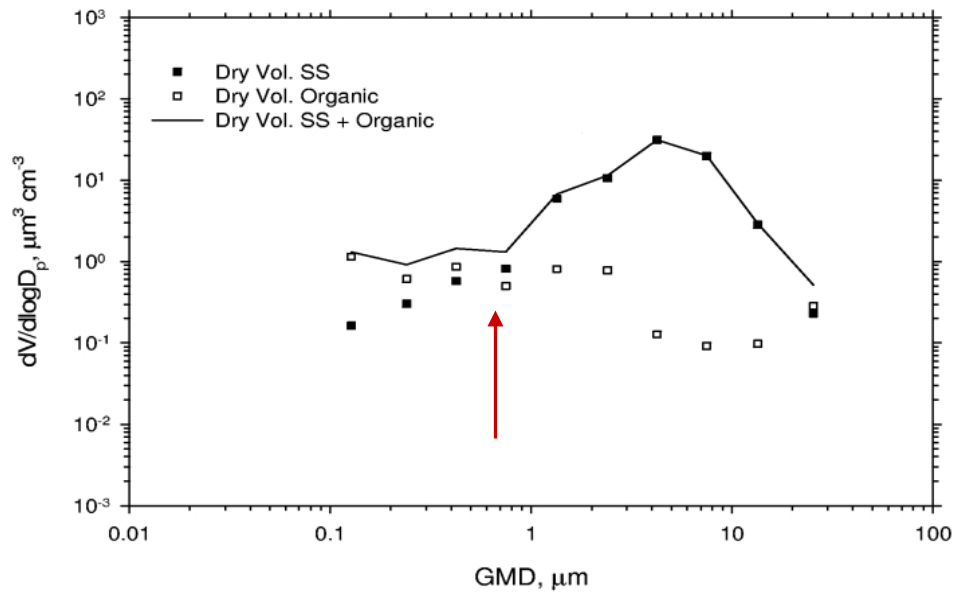
Calculated



$D_p, \mu\text{m}$ at RH=80%

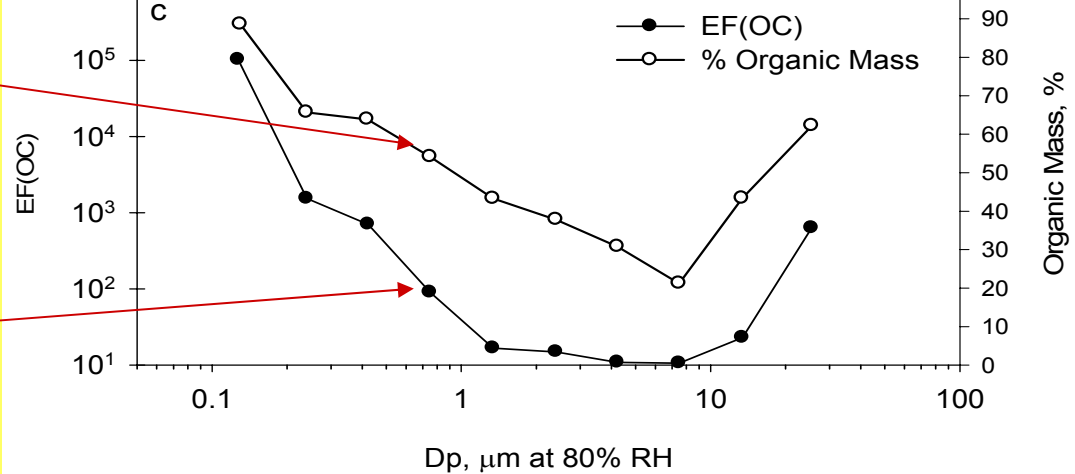
Production = $f(V_a)$

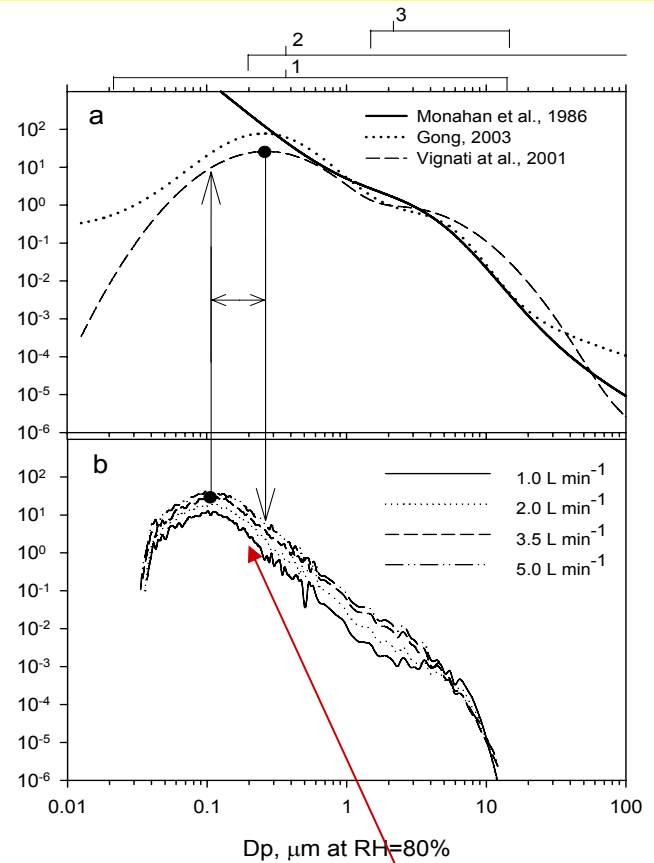
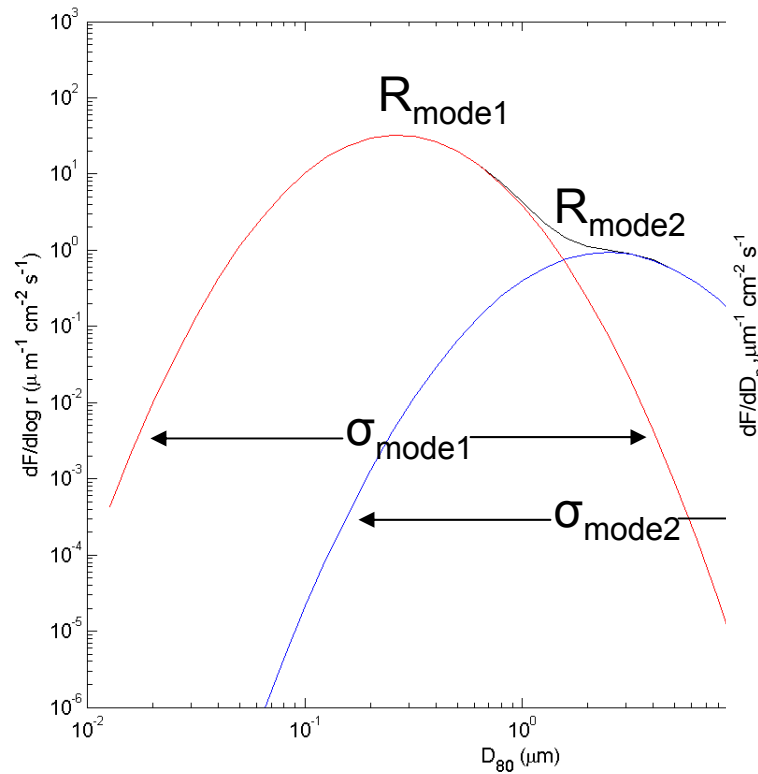




% Organic Mass

Organic Carbon (OC) Enrichment vs. bulk seawater





$$\log N_i = A_i \frac{\alpha}{\epsilon} \frac{V}{g} \frac{\partial}{\partial r} C B_i$$

$$r(\log r) = \frac{1}{P_i(r)}$$

$$P_i(\log r) = \sqrt{2p \log s_i} \exp \left[\frac{\alpha}{\epsilon} \frac{K}{C} \frac{(\log r - K \log R_i(g))^2}{2 \log^2 s_i} \right]$$

U → ***Wave Development***

→ ***Dissipation***

→ ***Wave Breaking***

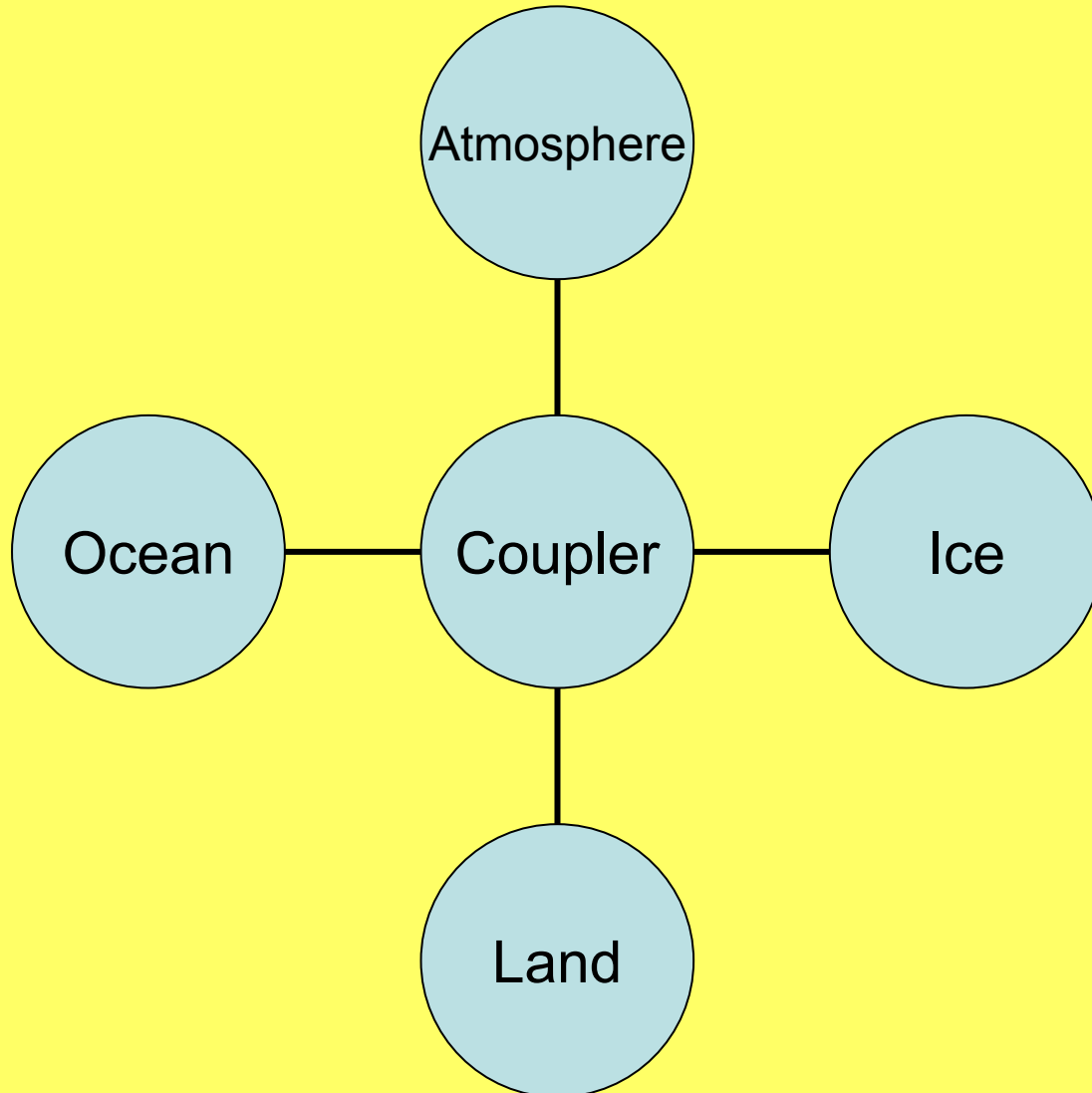
$$E_T = E_{IN} + E_{NL} + E_D$$

$\frac{AE_D}{\rho g \lambda}$ → ***Air Entrainment***

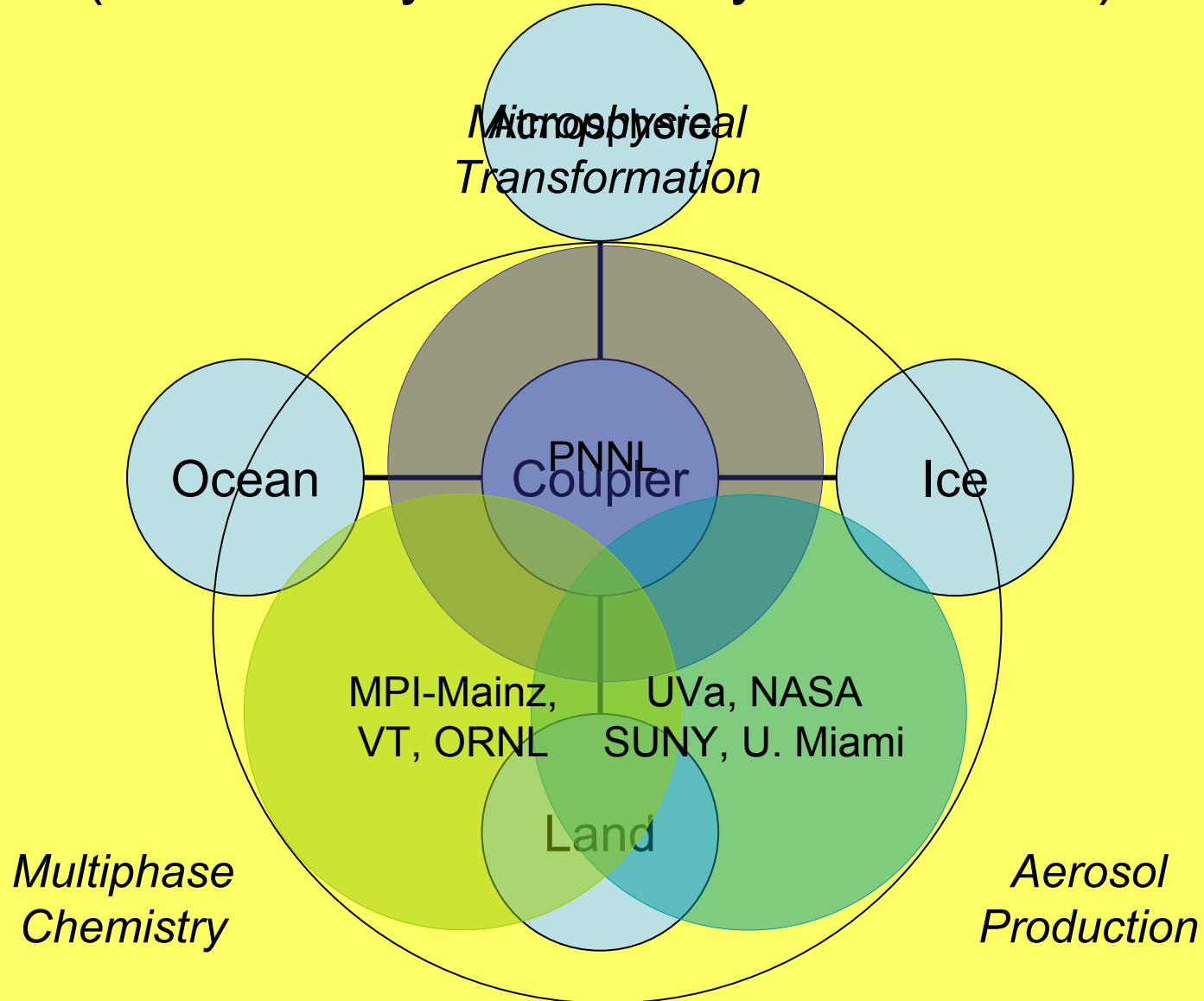
→ ***Particle Production***

$$\log N_i = A_i \frac{v_a^3}{g} \frac{a}{\phi} C B_i$$

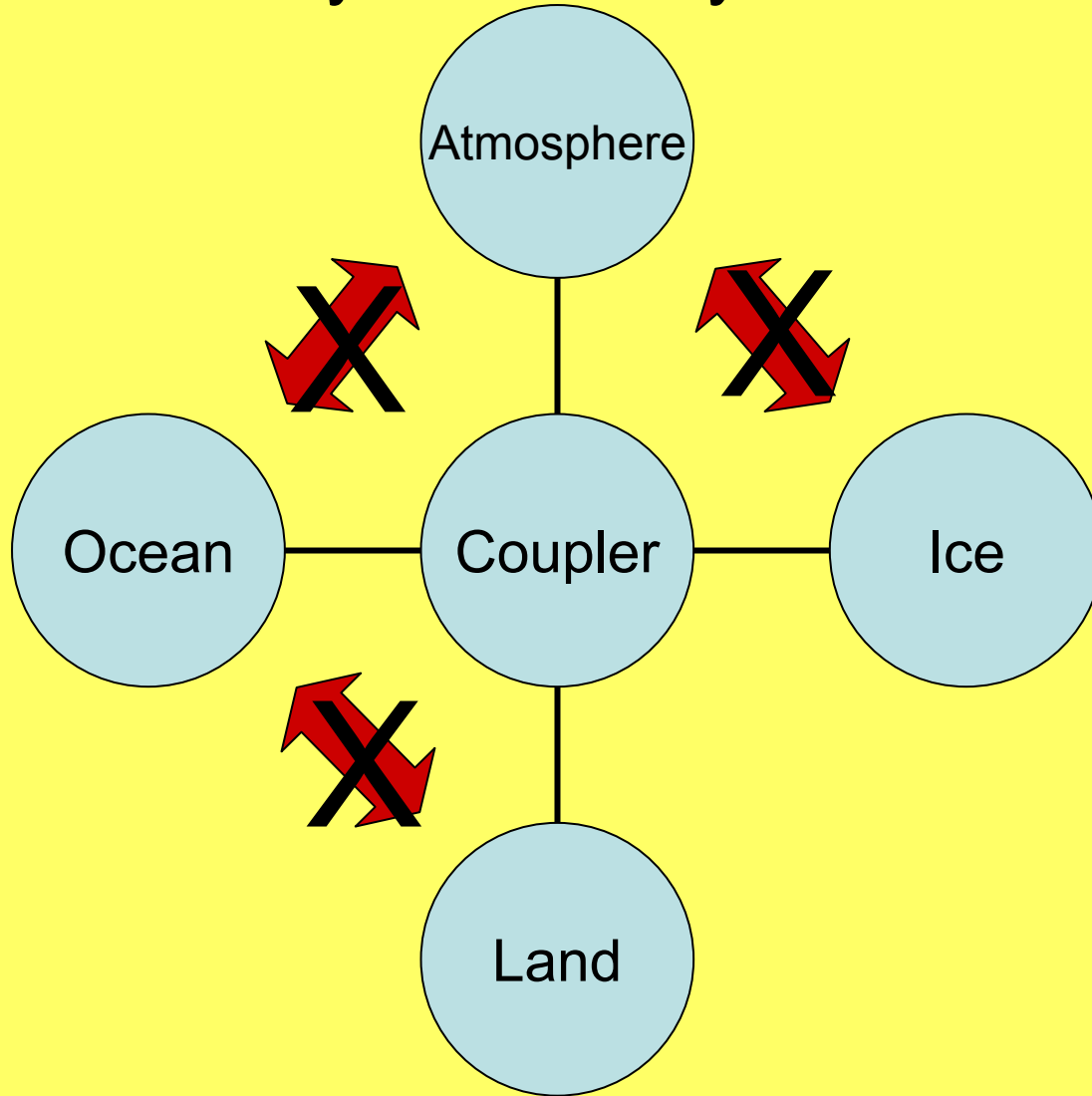
Interface with Global Climate Model (Community Climate System Model)



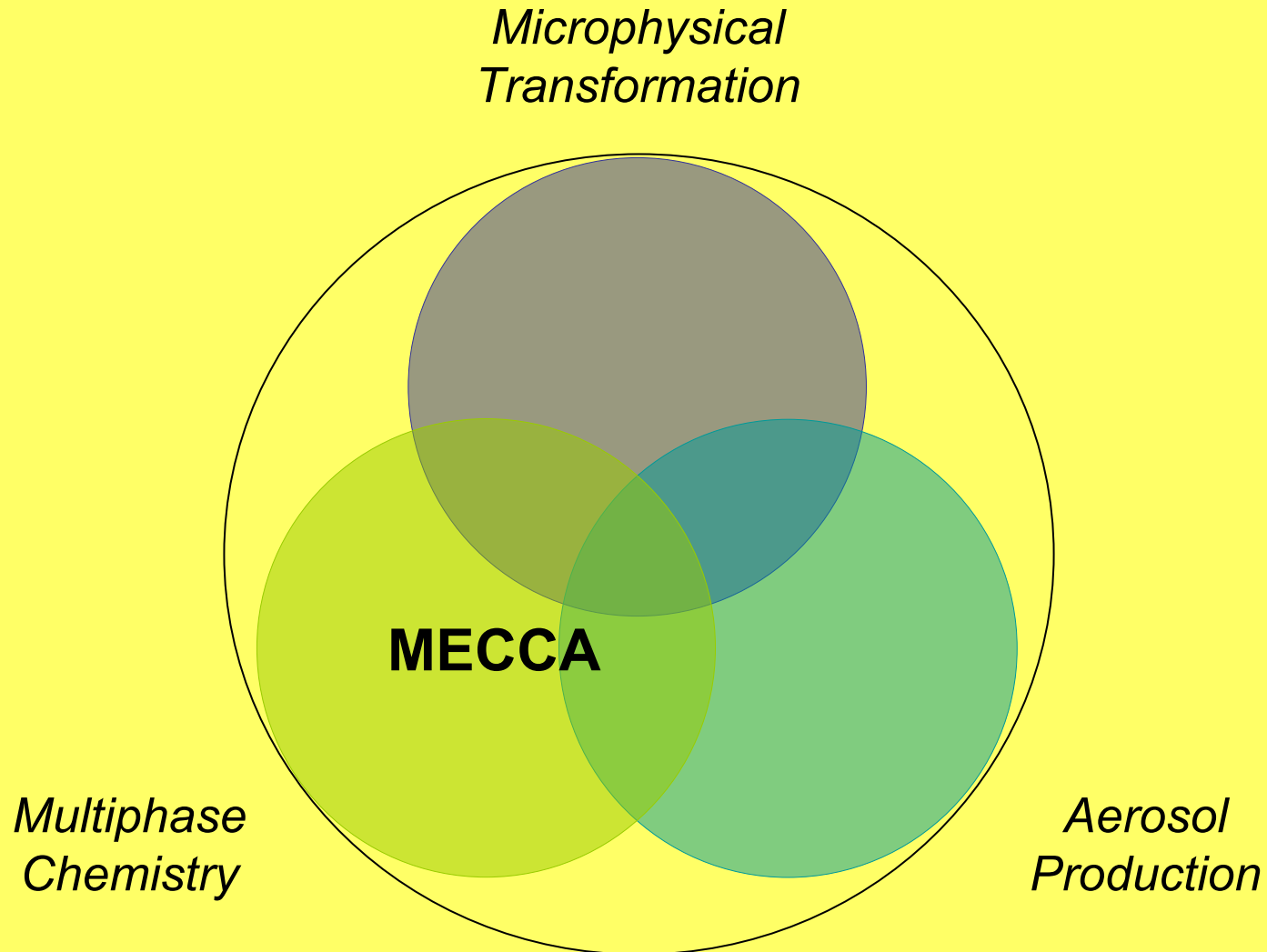
Interface with Global Climate Model (Community Climate System Model)



Interface with Global Climate Model (Community Climate System Model)



Interface with Global Climate Model (Community Climate System Model)



MECCA

(Module Efficiently Calculating the Chemistry of the Atmosphere).

Atmospheric chemistry models

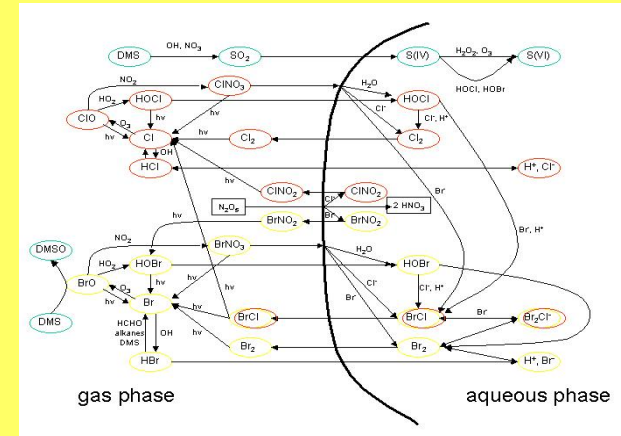
Vary in complexity and efficiency.

Often fit niches (e.g. tropospheric or stratospheric)

Often not purely chemical (e.g. include meteorology)

Subject to code-based incompatibilities.

...rendered unsuitable for general applications.



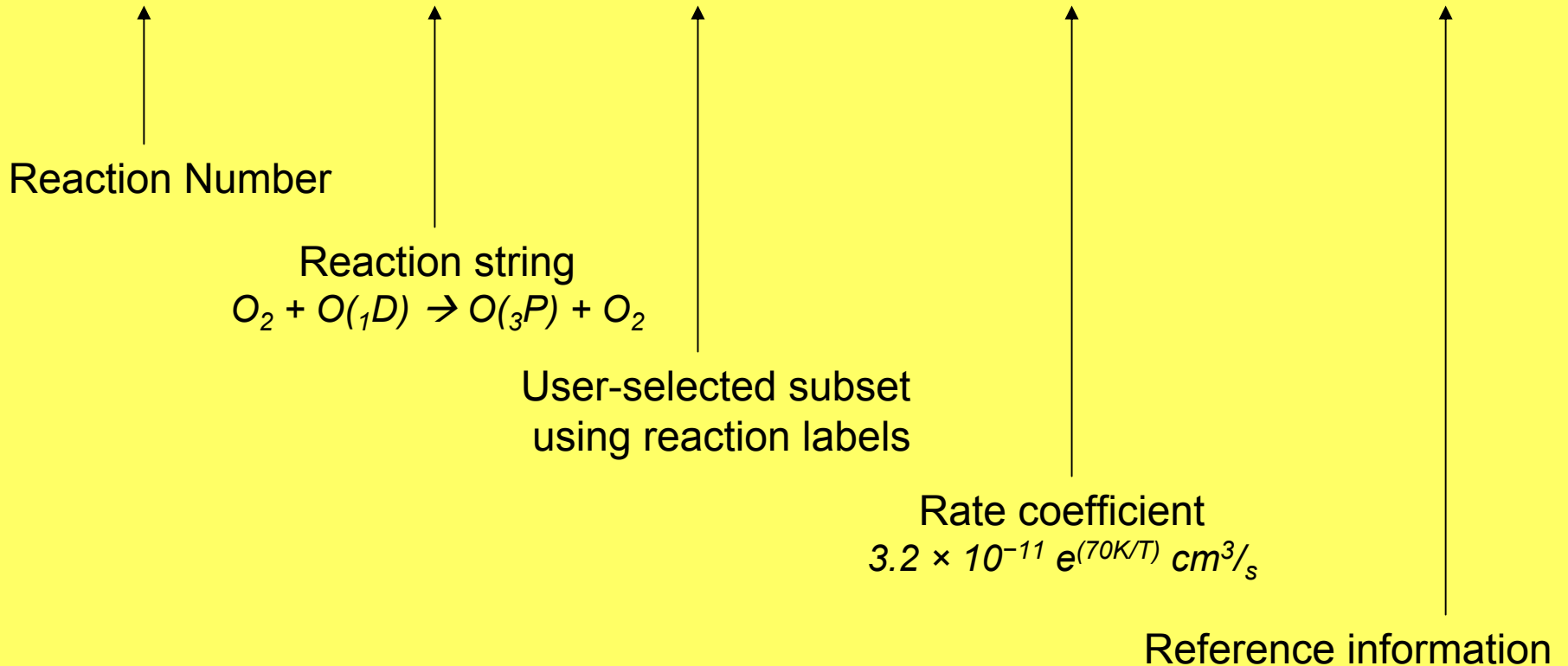
```
{1} CH3OH + OH = HO2 + HCHO : 6.01D-18*TEMP**2*EXP(170/TEMP)
      {2} 1.22D-11*0.493 ;{3} OH + PECO2 = PE2ENEBO2 :
      {4} 1.22D-11*0.070 ;{4}
      {5} 1.22D-11*0.436 ;{5}
      {6} J(2) ;{6}
      {7} OH + HCHO = HO2 + CO : 1.20D-14*TEMP*EXP(287/TEMP) ;{7}
      {8} 5.80D-16 ;{8}
      {9} HCHO = CO + HO2 + HO2 : J(11) ;{9}
      {10} PE2ENEBO2 = C523OH : 8.80D-13*0.2*RO2 ;{10}
      {11} PE2ENEBO2 = MPRKAOH : 8.80D-13*0.2*RO2 ;{11}
      {12} PE2ENEBO2 = PE2ENEBO : 8.80D-13*0.6*RO2 ;{12}
      {13} PE2ENEBO2 + NO = PE2ENEBO3 : KRO2NO*0.064 ;{13}
      {14} PE2ENEBO2 + NO = PE2ENEBO + NO2 : KRO2NO*0.936 ;{14}
      {15} KRO2HO2*0.706 ;{15}
      {16} PE2ENEBO2 + NO3 = PE2ENEBO + NO2 : KRO2NO3 ;{16}
      {17} HO3CSO2 = HO3C4CHO : 1.30D-12*0.2*RO2 ;{17}
      {18} HO3CSO2 = HO3CSO : 1.30D-12*0.2*RO2 ;{18}
      {19} HO3CSO2 + NO = HO3CSNO3 : KRO2NO*0.052 ;{19}
      {20} HO3CSO2 + HO2 = HO3CSOOH : KRO2HO2*0.706 ;{20}
      {21} HO3CSO2 + NO = HO3CSO + NO2 : KRO2NO*0.948 ;{21}
      {22} HO3CSO2 + NO3 = HO3CSO + NO2 : KRO2NO3 ;{22}
      {23} DIEK + OH = DIEKAO2 : 2.00D-12*0.501 ;{23}
      {24} DIEK + OH = DIEKBO2 : 2.00D-12*0.499 ;{24}
      {25} DIEK = C2H5CHO + C2H5O2 : J(22) ;{25}
      {26} C523OH + OH = DIEKAOH + HO2 : 2.14D-11 ;{26}
      {27} MPRKAOH + OH = CO2C3S + HO2 : 1.00D-11 ;{27}
      {28} MPRKAOH = C2H5CHO + CH3CO3 + HO2 : J(22) ;{28}
      {29} PE2ENEBO = CH3CHO + C2H5CHO +
      {30} HO2 : 2.00D+14*EXP(-4714/TEMP) ;{30}
      {31} PE2ENEBO3 + OH = MPRKAOH + NO2 : 3.25D-12 ;{31}
      {32} C53OH2OOH = PE2ENEBO + OH : CS3OH2OOH = PE2ENEBO + OH :
      {33} 1.90D-12*EXP(190/TEMP) ;{33}
      {34} C53OH2OOH + OH = MPRKAOH + OH : 3.19D-11 ;{34}
      {35} OH + HO3C4CHO = HO1C03C5 + HO2 : 1.61D-11 ;{35}
      {36} HO3C4CHO = HO3C4CO3 + HO2 + CO : 5.56D-11*0.389 ;{36}
      {37} : 5.56D-11*0.611 ;{37}
      {38} NO3 + HO3C4CHO = HO3C4CO3 + HNO3 : KNO3AL*5.5 ;{38}
      {39} : 2.03D+11*EXP(-3430/TEMP) ;{39}
      {40} OH + HO3C5NO3 = HO3C4CHO + NO2 : 1.20D-11 ;{40}
      {41} : J(53) ;{41}
      {42} OH + HO3C5OOH = HO3C5O2 : 1.90D-12*EXP(190/TEMP) ;{42}
      {43} OH + HO3C5OOH = HO3C4CHO + OH : 2.28D-11 ;{43}
```

What about MECCA?

Chemical flexibility

Only one master file with all reactions...

<G1000> O2 + O1D = O3P + O2 : {%StTrG} %3.2E-11*EXP(70./temp); {&1555}



What about MECCA?

Numerical flexibility

Kinetic Preprocessor (KPP)...

Solves the concentration time derivative of a given chemical system

Suite of Implicit ODE solvers, e.g.:

RADAU5: *Runge Kutta method, slow, accurate*

ROS2: *Rosenbrock method, manual time step control, fast*

ROS3: *Rosenbrock method, automatic time step control, robust suitable for very stiff systems*

Project Objectives

Mechanistic / Model Development

Merge the new *marine aerosol production* algorithm into the *CCSM*.

Incorporate suitably reduced wave dynamics into wind-driven aerosol production.

Refine/extend production function with new experimental data... (i.e., pending proposal for shipboard deployment of generator).

Test and benchmark *MECCA* in *3-D* framework

- *Across a relevant scope of multiphase chemical regimes*
- *Determine dominant reaction modes*
- *Evaluate interface with model physics*

Tune and *optimize KPP* in *multiphase and global* settings

- *Efficiency vs. Accuracy*
- *Stability vs. Stiffness*

Project Objectives

Atmospheric Chemistry and Climate-relevant Science Questions

Evaluate the importance of *OC content of seawater* to the global *marine aerosol burden and composition*.

Evaluate the relative *contribution of primary marine aerosol* to *CN and CCN* in the global marine troposphere.

Determine the *impact of primary marine aerosols on sulfur cycling* and associated climatic feedbacks.

Quantify variability in *halogen radical production* and its effect on *atmospheric oxidation and photochemical mechanisms* over global, regional and local scales.

Acknowledgements

Funding

- DOE – Office of Biological and Environmental Research
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- SciDAC
- University of Virginia – Dept. of Environmental Sciences

Collaboration

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- Oak Ridge National Laboratory
- Virginia Tech
- SUNY – Syracuse
- University of Miami
- National Center for Atmospheric Research (NCAR)
- Pacific Northwest National Laboratory
- NASA