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

A CCSM Development Study

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Role of aerosols in
Atmospheric Chemistry & Climate
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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)
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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
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**Chlorine Chemistry**

\[ \text{HNO}_3 + \text{Cl}^- \rightarrow \text{HCl(aq)} + \text{NO}_3^- \]

\[ \text{HOCl} + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \]

**Bromine Chemistry**

\[ \text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O} \]

\[ \text{HOCl} + \text{Br}^- + \text{H}^+ \rightarrow \text{BrCl} + \text{H}_2\text{O} \]

[\text{BrCl} + \text{Br}^- \rightarrow \text{Br}_2 + \text{Cl}^-]

\[ \text{HCl(aq)} \rightarrow \text{HCl(g)} \]

\[ \text{BrCl(aq)} \rightarrow \text{BrCl(g)} \]

\[ \text{Br}_2(aq) \rightarrow \text{Br}_2(g) \]

\[ \text{HNO}_3 + \text{Cl}^- \rightarrow \text{HCl(aq)} + \text{NO}_3^- \]

\[ \text{HOCl} + \text{Br}^- + \text{H}^+ \rightarrow \text{BrCl} + \text{H}_2\text{O} \]

\[ \text{BrCl} + \text{Br}^- \rightarrow \text{Br}_2 + \text{Cl}^- \]

HCl, Cl₂ → NMHC → O₃, OH, HO₂

[Sander and Crutzen, 1996; Sander et al., 2003]
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Sulfur Chemistry

S(IV) Oxidation

\[
\begin{align*}
\text{S(IV)} & \quad \to \quad \text{HOBr} \\
& \quad \to \quad \text{HOCI} \\
& \quad \to \quad \text{O}_3 \\
& \quad \to \quad \text{H}_2\text{O}_2
\end{align*}
\]

S(VI) Uptake

\[
\begin{align*}
\text{H}_2\text{SO}_4(g) & \quad \to \quad \text{HSO}_4^- + \text{H}^+ \quad \to \quad \text{SO}_4^{2-} + 2\text{H}^+ \\
\text{CH}_3\text{SO}_3\text{H}(g) & \quad \to \quad \text{CH}_3\text{SO}_3^- + \text{H}^+
\end{align*}
\]

DMS + BrO \to DMSO + Br

[Keene et al., 1998; von Glasow & Crutzen, 2004]
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CH2I2, CH2IBr
CH3I, CH3Br
CHBr3, CH2ICl

NOT SO SIMPLE!
Bubble bursting

Film Droplets

Jet Droplets
\[ N(D_p) = F(D_p)_{up} - F(D_p)_{down} \]
Dp, μm at RH=80%

Monahan et al., 1986
Gong, 2003
Vignati et al., 2001
Production = f($V_a$)

![Graph showing production as a function of bubble rate and diameter distribution.](image)

**Production = f($V_a$)**

Production is illustrated in the graph as a function of bubble rate, with data points representing different bubble rates and media types (Water and Air). The graph includes best-fit lines for various experimental conditions.

Two modes of production are indicated, with one mode characterized by a higher density of particles at lower bubble rates and the other mode showing a broader distribution at higher bubble rates. The graph also includes data from different studies: Monahan et al., 1986; Gong, 2003; Vignati et al., 2001.

The graph further shows the relationship between diameter distribution ($dF/dD_p$) and number concentration ($dN/dD_p$), with the x-axis representing diameter in nm and the y-axis representing number concentration per cm$^2$ sec$^{-1}$. The graph highlights two distinct modes of production, with different scales for low and high bubble rates.
Organic Carbon (OC) Enrichment vs. bulk seawater

% Organic Mass

Dp, μm at 80% RH
\[
\log N_i = A_i \frac{V_a}{e} \frac{\sigma}{g} \frac{C}{e} B_i \] 
\[
R_i(r) = \sum_{i=1}^{\infty} P_i(r) 
\]
\[
P_i(\log r) = \sqrt{2p \log s_i} \exp \frac{\alpha}{e} K \left( \log r \frac{K}{2} \log \frac{R_i(g)}{s_i} \right) \]
$U \rightarrow \text{Wave Development}$

$\rightarrow \text{Dissipation}$

$\rightarrow \text{Wave Breaking}$

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

$\frac{A E_D}{\rho g \lambda} \rightarrow \text{Air Entrainment}$

$\rightarrow \text{Particle Production}$

$log N_i = A_i \frac{a}{e g \phi} C B_i$
Interface with Global Climate Model (Community Climate System Model)
Interface with Global Climate Model (Community Climate System Model)

Microphysical Transformation

Ocean

PNNL Coupler

Ice

MPI-Mainz, VT, ORNL
UVa, NASA
SUNY, U. Miami

Multiphase Chemistry

Land

Aerosol Production
Interface with Global Climate Model (Community Climate System Model)
Microphysical Transformation

Interface with Global Climate Model (Community Climate System Model)

MECCA

Multiphase Chemistry

Aerosol Production
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.
What about MECCA?

Chemical flexibility

Only one master file with all reactions...

\[ \text{Reaction Number} \]

\[ \text{Reaction string} \]

\[ O_2 + O(1D) \rightarrow O(3P) + O_2 \]

User-selected subset using reaction labels

Rate coefficient

\[ 3.2 \times 10^{-11} \ e^{(70K/T)} \ cm^3/s \]

Reference information
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
• National Science Foundation
• SciDAC
• University of Virginia – Dept. of Environmental Sciences

Collaboration

• Max Planck Institute for Chemistry
• Oak Ridge National Laboratory
• Virginia Tech
• SUNY – Syracuse
• University of Miami
• National Center for Atmospheric Research (NCAR)
• Pacific Northwest National Laboratory
• NASA