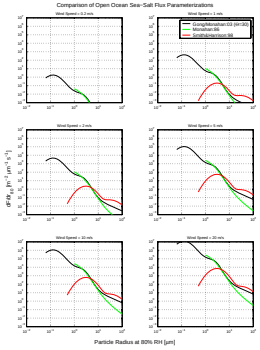
Initial Applications of Sea Salt Aerosol Emissions and Chemistry Algorithms in the CMAQ v4.5 – AERO4 Module

Background

• **2004:** K. M. Zhang and P. V. Bhave adapted sea salt emissions code of G. Pouliot based on the parameterization of Smith and Harrison (1998; SH98) to the CMAQ-UCD sectional aerosol model; updated open-ocean source function to follow Gong (2003); treated RH dependence of emitted size distribution (Zhang et al., 2005).

• **2004-05**: Cooperative agreement of U.S. EPA and UNC-CEP to incorporate sea salt emissions and chemistry into the standard CMAQ modeling framework (modal approach); entailed a detailed comparison of various flux parameterizations, development of a methodology to apportion the emissions among the modes, implementation of the emissions calculation on-line in CMAQ, and addition of sea salt species to the aerosol module. These changes have been integrated into CMAQ v4.5 and released in the AERO4 aerosol module.

Emission Modeling



Comparison of Flux Parameterizations

In the left panels, the parameterized fluxes are plotted only within the size ranges of validity, as reported in the original studies.

Key: SH98 - Smith and Harrison (1998)
M86 - Monahan et al. (1986); shown in several studies to perform better than SH98 below 10 μm radius at 80% RH (r_{80}); valid for r_{80} above 1 μm
GM03 - Extension of M86 to submicron sizes (r_{80} > 0.06 μm) by S. L. Gong (2003)

GM03 and M86 agree closely for r_{80} = 1.0 - 10 μm, because GM03 is adapted from M86 in this size range. GM03 is the only function valid for r_{80} < 1.0 μm.

GM03 was thus selected as the source function in CMAQv4.5.

GM03 source function:

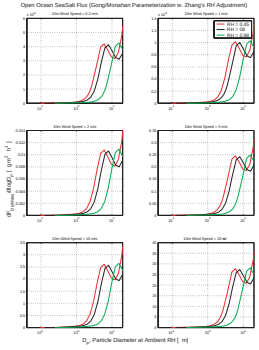
$$\frac{dF}{dr_{80}} = 1.373\, u_{10}^{3.41} r_{80}^{-A} (1 + 0.057 r_{80}^{3.45}) 10^{B\exp(-(0.433 - \log r_{80})^2/0.433)}$$

with u_{10} = the wind speed at 10-m height;

$A = 4.7 \cdot (1 + \Theta r_{80})^{-0.017 r_{80}^{-1.44}}$, with $\Theta = 30$; and

$B = (0.433 - \log r_{80})/0.433$

Zhang et al. (2005) have provided a correction to r_{80} to extend range of applicability of these parameterizations to RH between 45% and 99%, as shown in the right panels.

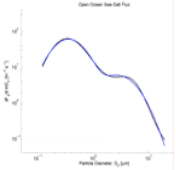


Flux Integration and Lognormal Fitting for Modal Emission Splits

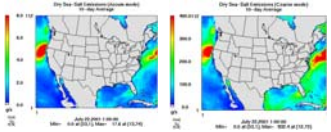
To integrate the fluxes, GM03 (black curve) has been fit to a bimodal lognormal distribution (blue curve) using 3 parameters each in the accumulation and coarse modes for the range of RH:
N - the particle number concentration
$D_{g,n}$ - the geometric number median diameter, and
σ_g - the geometric standard deviation.

N.B.: Coarse-mode σ_g held constant at 2.2

Parameter values for RH from 0 – 99% are stored in a look-up table, and interpolated to **ambient RH** to integrate the fluxes over the appropriate size range. Volume fractions apportioned to each mode are calculated from truncated lognormals for better accuracy, using the min and max diameters at ambient RH in each grid cell (based on the range of validity of 0.06 - 10 μm dry diameters for GM03) .



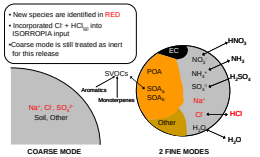
Emissions Diagnostic File Output



Note the difference in scale between accumulation- and coarse-mode sea salt (factor of 50).
At the point of emission, most of sea-salt mass is in the coarse mode.

Chemistry Modeling and Results

Sea Salt Species Added in CMAQ

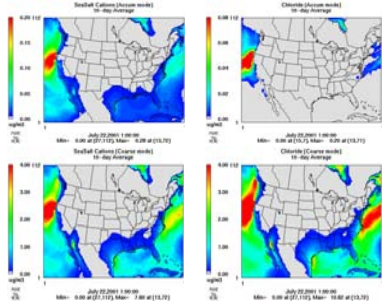


Test Simulations

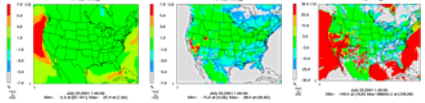
Model Configuration:
July 22-31, 2001
36 km ConUS domain, 14 vertical layers
ICs from OAQPS v4.4 run
BCs from GEOS-CHEM global model
ICs & BCs contain no sea salt

Results (right panels):
Sea-salt cations consist of 78% Na plus small amounts of Mg, Ca, and K.
Note the differences in scale.
Although chloride emissions exceed cations by 40%, cations are non-volatile, so their concentrations exceed those of Cl.

Ambient Concentrations



Effect of Sea Salt on Other Species

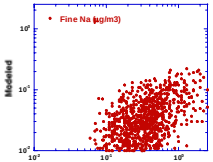


SO_4 increases over oceans, due to primary SO_4 in sea salt. Relative change over the continent is less than 1%. Absolute changes are small (< 0.1 μg/m³).

NH_4 decreases over oceans due to competition with sea-salt cations for SO_4 and NO_3. Decrease over eastern U.S. is minor (< 0.1 μg/m³ absolute change), and appears to be due to a reduction in the atmospheric NH_3 budget driven by enhanced deposition. All absolute changes are small (< 0.1 μg/m³).

NO_3 increase over oceans, due to condensation of HNO_3 on to sea-salt particles. This increase penetrates into California. The increase in Utah is likely because nitrate formation was ammonia limited. Decrease over Midwest is minor (< 0.1 μg/m³ absolute change), and appears to be due to a decrease in TNO_3 (not due to change in gas-particle partitioning), driven by enhanced deposition. Relative differences are large, because total nitrate is very low in summer.

Comparisons with IMPROVE in Coastal States from Annual 2001 Simulation



- Na acts as a passive tracer; is thus useful for checking correctness of sea salt emissions.
- Underpredicted by a factor of 2-10 at most sites. Possibly due to:
  - underestimation of fine Na emissions; mass flux is mostly in coarse particles
  - sampling inlet not having an exact cut-off at 2.5 μm, as with model output
  - possible source of Na besides sea salt
  - surf zone emissions not included; lower tail of coarse mode (< 2.5 μm) in surf zone may contribute significantly in coastal areas.

Future Work

- Surf zone source function will be included in CMAQ v4.6
- There is a lack of reliable network observations for Na and Cl. Will compare with intensive field campaigns (e.g., BRACE, Pacific Northwest) and NADP data for total deposition
- Coarse mode chemistry will be added in CMAQ v4.6
- May include heterogeneous Cl_2 production and new gas-phase chloride mechanism, and the linkages to the CMAQ Hg model

References

Gong, S.L, *Global Biogeochem. Cycles, 17*(4), 1097, doi:10.1029/2003GB002079, 2003.
Monahan, E. C., et al., A model of marine aerosol generation in whitecaps and wave dispersion. In *Oceanic Whitecaps and Their Role in Air-Sea Exchange,* E. C. Monahan and G. M. Niocaill (eds.), pp 167-174., D. Riedell, Norwell, Mass., 1986.
Smith, M. H., and N. M. Harrison, *J. Aerosol Sci., 29, Suppl. 1*, S189-S190, 1998.
Zhang, K. M., et al., *Atmos. Environ. 39*, 3373-3379, 2005.

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ushankar@unc.edu
http://www.cep.unc.edu/empd

U. Shankar[1], P. V. Bhave[2] , J. M. Vukovich[3], and S. J. Roselle[2]

[1] Carolina Environmental Program, University of North Carolina at Chapel Hill, [2]NOAA (on assignment to EPA - NERL), [3]Baron Advanced Meteorological Systems