Final Report

Title: Process Models of the Equilibrium Size & State of Organic/Inorganic Aerosols for the Development of Large Scale Atmospheric Models & the Analysis of Field Data
Project ID: 0014056
PI: Anthony S. Wexler

Our work addressed the following elements of the Call for Proposals: (i) **"to improve the theoretical representation of aerosol processes studied in ASP laboratory or field studies"**,

(ii) **"to enhance the incorporation of aerosol process information into modules suitable for large-scale or global atmospheric models"**, and

(iii) **"provide systematic experimental validation of process model predictions ... using data from targeted laboratory and field experiments"**.

Achievements to the end of 2012 are described in four previous reports, and include: new models of densities and surface tensions of pure (single solute) and mixed aqueous solutions of typical aerosol composition under all atmospheric conditions (0 to 100% *RH* and $T > 150$ K); inclusion of these models into the widely used Extended Aerosol Inorganics model (*E-AIM*, http://www.aim.env.uea.ac.uk/aim/aim.php); the addition of vapor pressure calculators for organic compounds to the *E-AIM* website; the ability of include user-defined organic compounds and/or lumped surrogates in gas/aerosol partitioning calculations; the development of new equations to represent the properties of soluble aerosols over the entire concentration range (using methods based upon adsorption isotherms, and derived using statistical mechanics), including systems at close to zero *RH*. These results are described in publications 1-6 at the end of this report, and on the "News" page of the *E-AIM* website (http://www.aim.env.uea.ac.uk/aim/info/news.html).

During 2012 and 2013 we have collaborated in a combined observation and lab-based study of the water uptake of the organic component of atmospheric aerosols (PI Gannet Hallar, of the Desert Research Institute). The aerosol samples were analyzed using several complementary techniques (GC/MS, FT-ICR MS, and ion chromatography) to produce a very complete organic "speciation" including both polar and non-polar compounds. Hygroscopic growth factors of the samples were measured, and we have just completed comparisons of the data with our process model predictions based upon the inorganic and organic composition of the samples. This directly addresses element (iii) of the Call for Proposals. The overview paper for this project is publication 7 below, and our work on the model comparisons will be written up over the next two months.

Impact

The best single measure of the impact of our ASR-funded work is the record of individual calculations carried out by users of the models on the *E-AIM* website. The table below shows annual usage of the model up to 31 December 2012. There have been steady increases over the last 4 or 5 years as more capabilities have been added, partly under ASR funding, and the last two years show a very large increase in overall usage of the model relative to 2010 (see the column headed "**All**").

Year	All	E-AIMTr	E-AIM25	Density	Di-acid	VapourP	ACCENT	DensAqu	SurfTen
98	3334	2921	413	-	-	-	-	-	0
99	17597	12820	4777	-	-	-	-	-	0
00	11759	10569	1190	-	-	-	-	-	0
01	15674	13542	2132	-	-	-	-	-	0
02	11453	9042	2411	-	-	-	-	-	0
03	11772	7807	3965	-	-	-	-	-	0
04	11788	7763	4025	-	-	-	-	-	0
05	12901	9422	3479	-	-	-	-	-	0
06	6067	4143	1924	-	-	-	-	-	0
07	15059	8754	6305	-	-	-	-	-	0
08	14354	7946	6408	-	-	-	-	-	0
09	20682	9238	8744	582	961	1157	-	-	0
10	23702	8728	10169	972	1066	1786	264	233	484
11	48474	32926	7683	1590	759	1393	140	719	1279
12	146327	123097	7759	1457	560	4316	307	528	3688

This very large increase is due in part to automated calls of the model from Harvard University, the California Air Resources Board, and the Swiss Federal Institute of Technology (ETH Zurich).

Publications

(1) C. S. Dutcher, A. S. Wexler, and S. L. Clegg (2010) Surface tensions of inorganic multicomponent aqueous electrolyte solutions and melts. *J. Phys. Chem. A* **114**, 12216-12230.

(2) S. L. Clegg and A. S. Wexler (2011) Densities and apparent molar volumes of atmospherically important electrolyte solutions. 1. The solutes H_2SO_4, HNO_3, HCl, Na_2SO_4, $NaNO_3$, NaCl, $(NH_4)_2SO_4$, NH_4NO_3, and NH_4Cl from 0 to 50 ^oC, including extrapolations to very low temperature and to the pure liquid state, and $NaHSO_4$, NaOH, and NH_3 at 25 ^oC. *J. Phys. Chem. A* **115**, 3393-3460.

(3) S. L. Clegg and A. S. Wexler (2011) Densities and apparent molar volumes of atmospherically important electrolyte solutions. 2. The systems H^+-HSO_4^--SO_4^{2-}-H_2O from 0 to 3 mol kg^{-1} as a function of temperature and H^+-NH_4^+-HSO_4^--SO_4^{2-}-H_2O from 0 to 6 mol kg^{-1} at 25 ^oC Using a Pitzer Ion Interaction Model, and NH_4HSO_4-H_2O and $(NH_4)_3H(SO_4)_2$-H_2O over the entire concentration range. *J. Phys. Chem. A* **115**, 3461-3474.

(4) C. S. Dutcher, Xinlei Ge, A.S. Wexler, and S.L. Clegg (2011) Statistical mechanics of multilayer sorption: Extension of the Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-deBoer (GAB) adsorption isotherms. *J. Phys. Chem. C* **115**, 16474-16487.

(5) C. S. Dutcher, Xinlei Ge, A.S. Wexler, and S.L. Clegg (2011) Statistical mechanics of multilayer sorption: 2. Systems Containing Multiple Solutes. *J. Phys. Chem. C* **116**, 1850-1864.

(6) C. S. Dutcher, X. Ge, A.S. Wexler, and S.L. Clegg (2012) An isotherm-based thermodynamic model of multicomponent aqueous solutions, applicable over the entire concentration range. *J. Phys. Chem. A.* **117**, 3198-3213.

(7) A. G. Hallar, D. H. Lowenthal, S. L. Clegg, V. Samburova, N. Taylor, L. R. Mazzoleni, B. K. Zielinska, T. B. Kristensen, G. Chirokova, I. B. McCubbin, Don Collins (2012) Chemical and Hygroscopic Properties of Aerosol Organics Study at Storm Peak Laboratory. *J. Geophys. Res.(Atmospheres)* **118**, 1-13, doi:10.1002/jgrd.50373.