Testing and Validation of CHEMMAP Model Algorithms

Deborah P. French McCay and Nicole Whittier
Applied Science Associates (ASA), Inc.
70 Dean Knauss Drive
Narragansett, RI 02882
Phone: 401-789-6224
Fax: 401-789-1932

The accuracy of the transport algorithms depend on the accuracy of the current data used and the specification of the random turbulent diffusion coefficients. The current data used in this study were produced by a hydrodynamic model (Muin and Spaulding 1997a, b; Swanson et al., 1998; Spaulding et al. 1999a,b; Sankaranarayanan and Spaulding, 2003) calibrated and validated to data from Narragansett Bay (Rhode Island, USA, Ward et al., 2002). This interconnected hydrodynamic and chemical fate model system has been used in other studies (e.g., Boehm et al., 2001; French McCay and Isaji, 2004). The turbulent diffusion algorithms in CHEMMAP have been scaled and validated by dye studies (Okubo and Ozmidov, 1970; French et al., 1997) and observations of dispersion of (purposefully) spilled emulsions (the Venezuelan product Orimulsion) in the Caribbean Sea (French et al., 1997).

The results of the evaporation algorithm for surface floating slicks were tested against experimental data from Kawamura and Mackay (1985, 1987), who conducted seven experiments using toluene, cyclohexane, hexane and dichloromethane, measuring evaporation rates of chemical volatilizing from a galvanized sheet-metal pan. To keep temperature constant and avoid any heat conduction from the ground, the pans were placed on Styrofoam boards. Temperature and wind conditions were recorded for the time of the particular experiment. Two experiments were conducted for each chemical, with the exception of hexane. CHEMMAP simulations were performed using the conditions of the experiments, i.e., volume of chemical, temperature (3-38^{o}C), and wind speed (various outdoor). The normal spreading algorithms in CHEMMAP were disabled and the chemical thickness held constant at that used in the pan experiments. Table 1 contains the results and Figure 1 shows a comparison of the experimental evaporation to the CHEMMAP-predicted evaporation. The agreement is good (Pearson r^2=0.421) and the linear regression through the data falls close to a 1:1 relationship (slope = 0.906, with standard error 8.16).

The entrainment and dissolution algorithms, which are also used in the companion oil spill model SIMAP, have been validated for spills where subsurface concentration data are available. In the oil model SIMAP, dissolution and volatilization of mono- and polynuclear aromatic hydrocarbons (PAHs) are estimated and predicted PAH concentrations agreed with measured values from field samples (French McCay 2003). We have not identified similar data for a pure chemical spill with which to perform a validation exercise.

Test runs with CHEMMAP and three commonly transported petrochemicals, benzene, toluene and styrene demonstrate model behavior. The conditions run were a constant wind speed of 3 m/sec or 8 m/sec and no background current, such that all the dispersion and transport would be wind-driven. Environmental conditions were: salinity, 30 ppt; water temperature 10^{o}C; and suspended sediment concentration 10 mg/L. Instantaneous releases at the water surface and at 5 m were simulated. The mass balances over time for these tests are in Figures 2-4. Figure 2 shows the typical behavior of a floating volatile chemical, benzene. If released at the water surface, some benzene dissolves, but most of the mass floats and immediately evaporates. When released at 5 m (subsurface, Figure 2), more benzene dissolves in the water as the buoyant liquid (as droplets) rises through the water column. However, more than 85% of the spilled mass reaches the surface and rapidly evaporates off. The behavior of toluene and styrene are similar, but with progressively smaller percentages dissolved as solubility decreases (solubility of benzene > toluene > styrene). Figures 3 and 4 show the percentage in the atmosphere (having evaporated from the surface slicks or volatilized from the water) for all three chemicals and the two wind speeds. With the same chemical, higher wind speed increases the rate of volatilization, as expected as the increased turbulence increase flux across the air-sea boundary.

Table 1. Measured and predicted percentage evaporated by 1 hour for chemicals held in a pan at the indicted thickness.

Experiment	Chemical Name	Thickness of Chemical in Pan (mm)	Evaporation (%) in 1 hr	
			Experimental	Model Predicted
1	Tolulene	23	22.5	22.3
2	Tolulene	23	17.0	21.3
3	Cyclohexane	22	34.4	30.0
4	Cyclohexane	22	34.4	28.9
5	Hexane	24	35.1	38.4
6	Dichloromethane	23	31.0	22.6
7	Dichloromethane	22	25.7	15.0

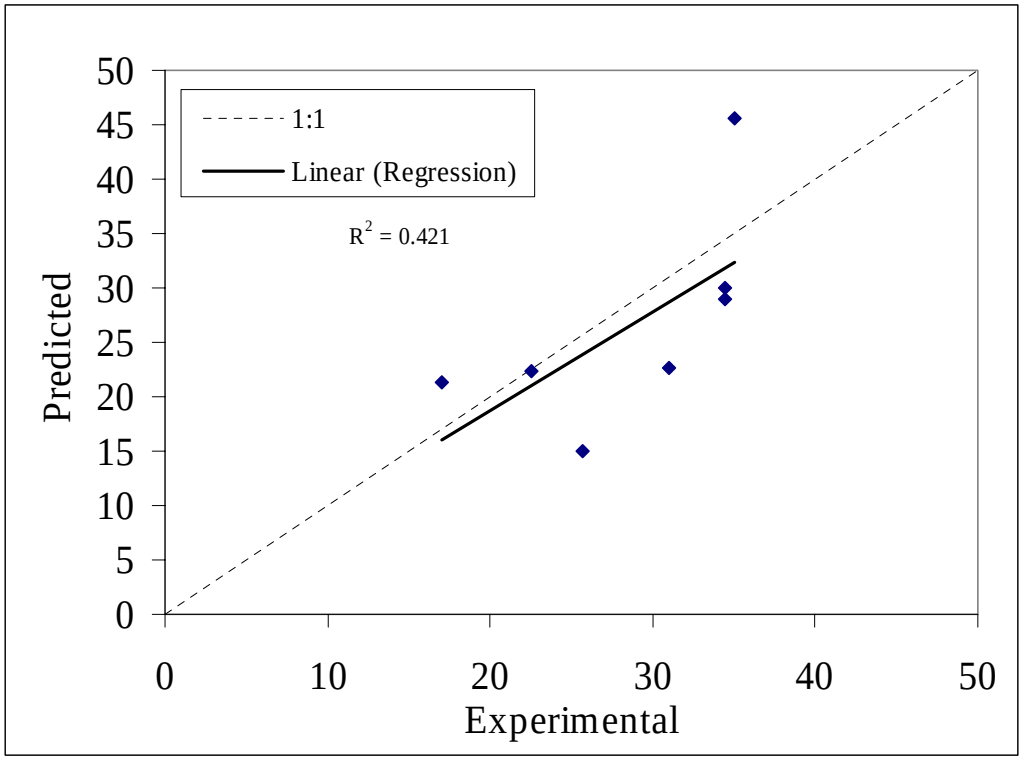


Figure 1. Comparison of measured and model-predicted percentage evaporated by 1 hour for four chemicals in seven experimental tests.

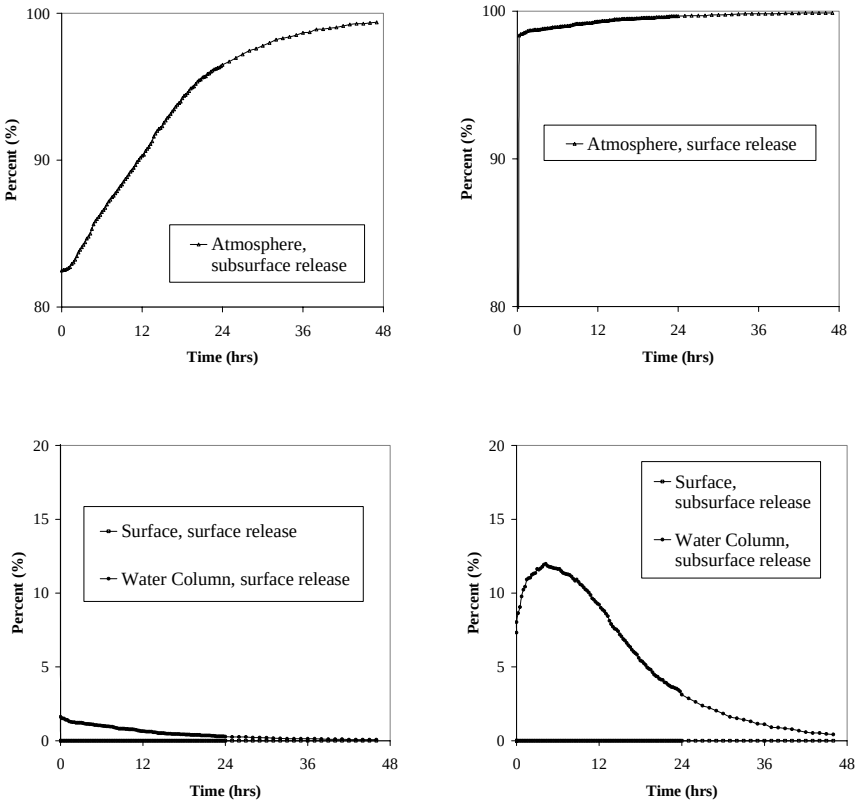


Figure 2. Mass balance over time for a 1000 MT release of benzene (wind speed 3 m/sec) at either the ater surface or at 5 m depth (subsurface).

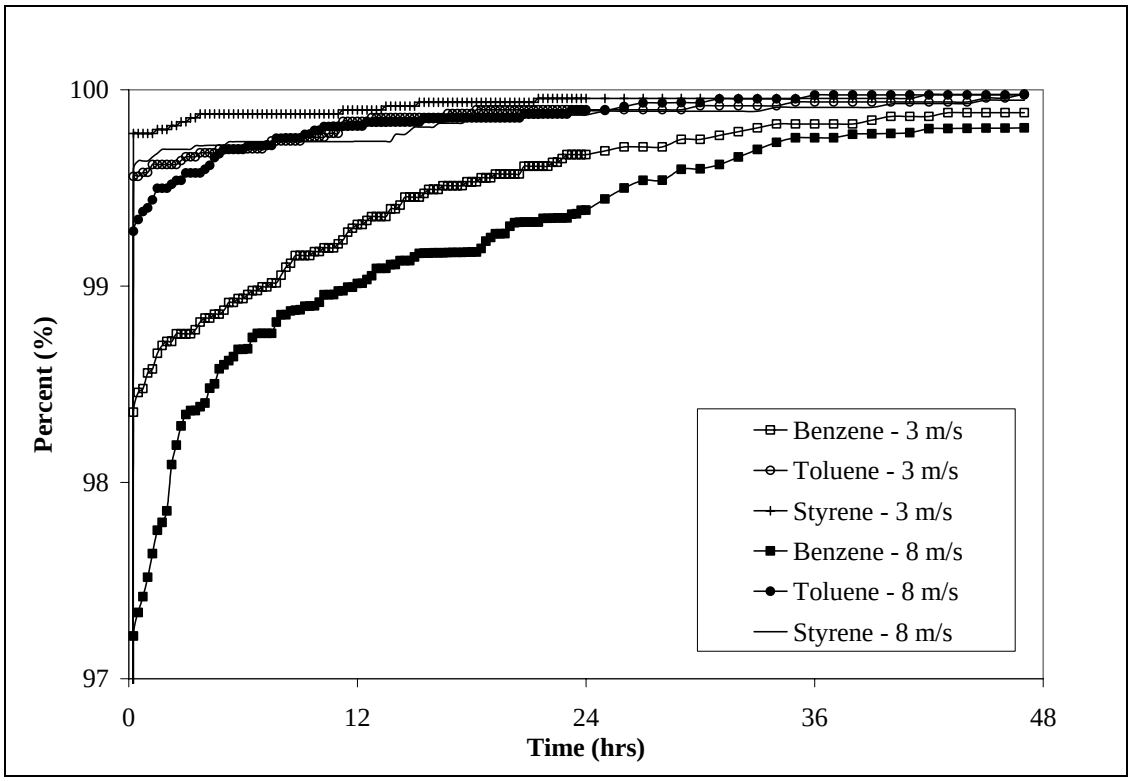


Figure 3. Percentage of the spilled mass volatilized to the atmosphere over time after an instantaneous release of 1000 MT at the water surface. (Wind speed indicated in the legend).

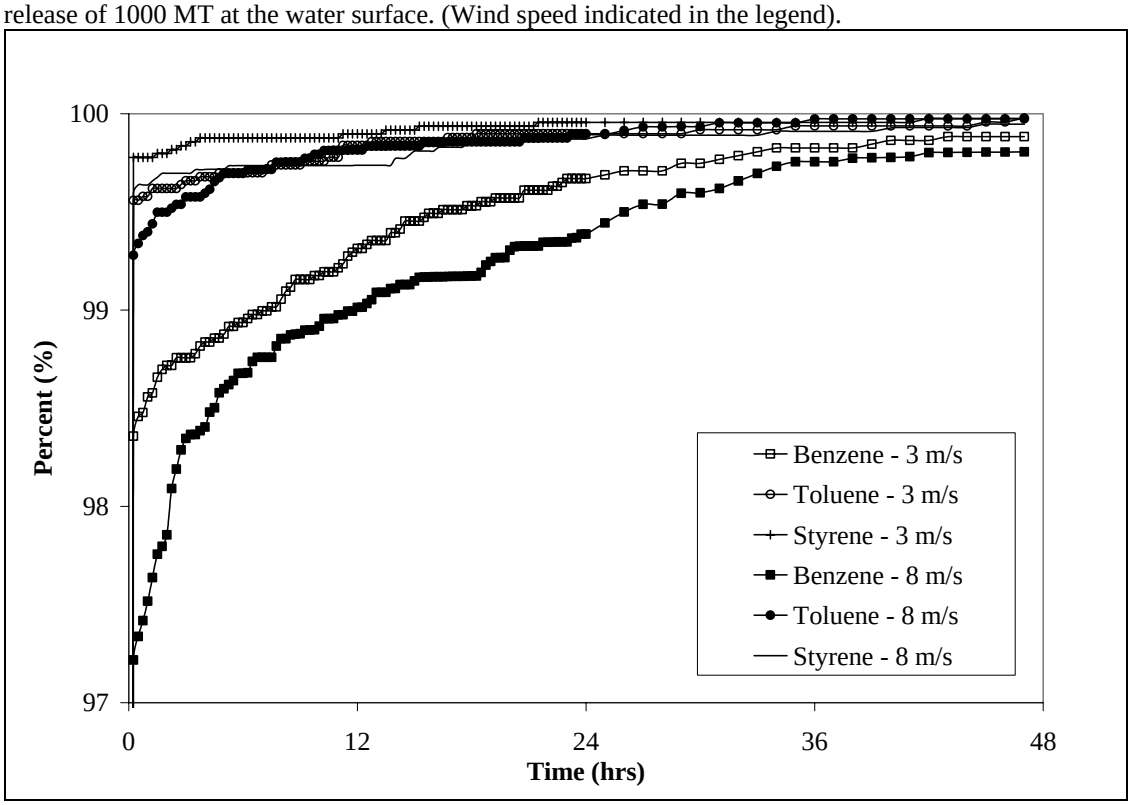


Figure 4. Percentage of the spilled mass volatilized to the atmosphere over time after an instantaneous release of 1000 MT at 5 m depth. (Wind speed indicated in the legend).

References:

Boehm, P., Turton, D., Raval, A., Caudle, D., French, D., Rabelais, N., Spies, R., Johnson, J., 2001. Deepwater Program: Literature Review, Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil & Gas Operations. Volume I, Technical Report. US Department of the Interior, Minerals Management Service (MMS), Gulf of Mexico OCS Region, OCS Study MMS 01-98-CT-30900, 326p.

French, D.P., Rines H. and Masciangioli, P., 1997. Validation of an Orimulsion spill fates model using observations from field test spills. In: Proceedings of the Twentieth Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Vancouver, Canada, June 10-13, 1997, Emergencies Science Division, Environment Canada, Ottawa, Ontario, Canada, pp.933-961.

French McCay, D.P., 2002. Development and application of an oil toxicity and exposure model, OilToxEx. Environmental Toxicology and Chemistry 21(10) 2080-2094.

French McCay, D.P. and Isaji, T., 2004. Evaluation of the consequences of chemical spills using modeling: chemicals used in deepwater oil and gas operations. Environmental Modelling & Software [in press, ENSO1408].

Kawamura, P.I. and Mackay, D., 1985. The evaporation of volatile liquids. Report EE-59, Technical Service Branch, Environment Canada, Ottawa, Ontario, Canada.

Kawamura, P.I. and Mackay, D., 1987. The evaporation of volatile liquids. Journal of Hazardous Materials 15: 343-364.

Muin, M. and Spaulding, M. 1997a. Three-dimensional boundary-fitted circulation model. Journal of Hydraulic Engineering 123(1).2-12.

Muin, M. and Spaulding, M. 1997b. Application of three-dimensional boundary-fitted circulation model to the Providence River. Journal of Hydraulic Engineering 123(1)13-20.

Okubo, A. and Ozmidov, R.V., 1970. Empirical dependence of the coefficient of horizontal turbulent diffusion in the ocean on the scale of the phenomenon in question. Atmospheric and Ocean Physics 6(5):534-53.

Sankaranarayanan, S., and Spaulding, M.L., 2003. A study of the effects of grid non-orthogonality on the solution of shallow water equations in boundary-fitted coordinate systems. Journal of Computational Physics 184(1):299-320.

Spaulding, M., Mendelsohn, D., and Swanson, J.C., 1999a. WQMAP: an integrated three-dimensional hydrodynamic and water quality model system for estuarine and coastal applications. Marine Technology Society Journal 33(3) 38-54.

Spaulding, M., Swanson, J.C., and Mendelsohn, D., 1999b. Application of quantitative model – data calibration measures to assess model performance. Estuarine and Coastal Modeling 6 (ECM6), New Orleans, Louisiana, 3-5 November 1999. American Society of Civil Engineers, Reston, Virginia, pp. 843-867.

Ward, M.C., Opishinski, T., Swanson, J.C., and French McCay, D., 2002. A globally re-locatable marine nowcast/forecast system. In: Proceedings, International Marine Environmental Seminar 2002, Trondheim, Norway.

Emergency Response Assistance and Validation for a Chemical Spill in an Undisclosed River

CLIENT: Confidential

A mixture of MIBK (methyl isobutyl ketone) and MEK (methyl ethyl ketone) were accidentally released through a once through cooling system into an undisclosed river. This river contained many branches, with some frozen off due to the cold weather. The branches that were not frozen then emptied into a lake.

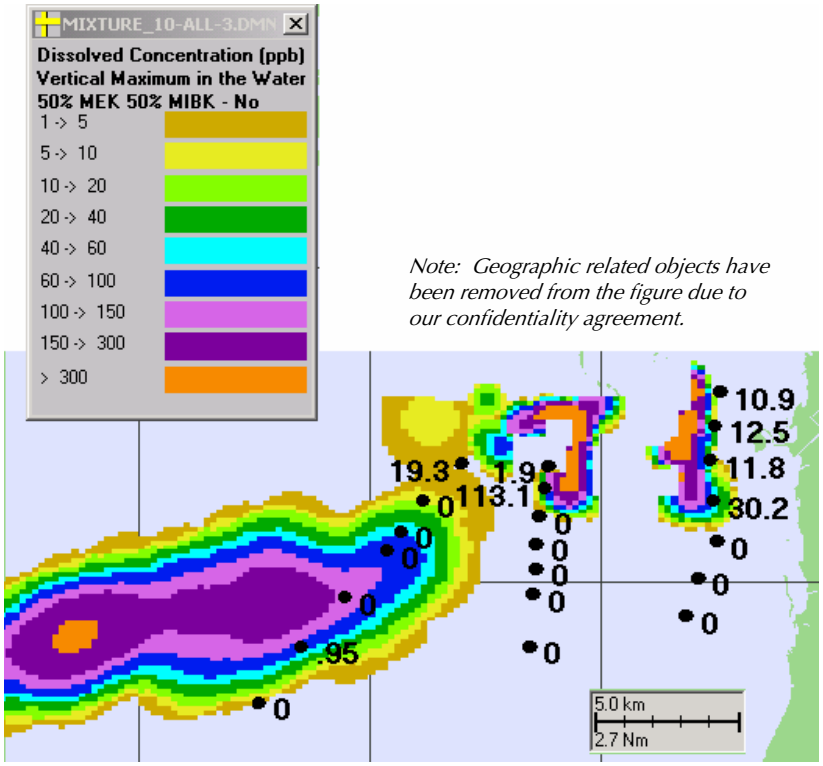
ASA was requested by the client to determine the trajectory and fate of the chemical throughout the multiple branches and lake. On-scene collected water column concentrations were used to validate and calibrate the chemical dispersion predictions.

ASA's chemical dispersion model, CHEMMAP, was used to determine the trajectory and fate of the chemical release. Generation of modeling parameters, such as hydrodynamic data, wind data, and chemical behavior, and locations of ice covering, were used to obtain results.

The CHEMMAP model prediction were then used by the client to determine sampling locations for the following day and to determine if any drinking water intake areas may be of concern for contamination. The model predictions were also used to determine when the chemical plume would dilute below detection limits, when this occurred the client could stop sampling. The sampling of the river and lake were required by the environmental agency.

During the modeling study the client provided samples taken for each day. These samples were used to calibrate and validate the model predictions. For the provided sampling data, all observed and CHEMMAP predicted concentration matched closely in location and concentration. The figure below depicts a series of sample data for one day compared to predicted concentrations. The points on the figure are the sampled points and the observed concentration in ppb. The color contours are the model predicted concentration. The colors refer to the key above the figure.

Please note, due to our confidentiality agreement we cannot disclose detailed information regarding this project. Therefore any geographical related objects have been removed from the figure and are not described in the project description.



Note: Geographic related objects have been removed from the figure due to our confidentiality agreement.

APPLIED SCIENCE ASSOCIATES, INC.

Headquarters:
Narragansett, RI
Phone: 401-789-6224
Fax: 401-789-1932
asa@appsci.com
www.appsci.com

Worldwide Offices:
Castetbon, France
St. Andrews, Scotland
São Paulo, Brazil
Gold Coast, Australia
Perth, Australia