

Modeling Pharmaceuticals and Organic Wastewater Chemicals

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Abstract:

A wide variety of pharmaceuticals and other organic wastewater chemicals are continuously being discharged in our streams and rivers. It is important to understand how the water quality will be effected from such discharges, how far will the chemical be transported as well as what are the potential concentrations in the water. To help address these needs, the three-dimensional chemical dispersion model CHEMMAP is used to estimate the fate and concentrations of selected organic wastewater chemicals, as well as the potential human health and ecological hazards from the discharged wastewater.

CHEMMAP uses environmental data forcing (currents and wind) and physical-chemical properties to simulate fate processes over time after the release, including: (1) slick spreading, transport, and entrainment of floating materials, (2) transport of dissolved and particulate materials in three dimensions, (3) evaporation and volatilization, (4) dissolution and adsorption, (5) sedimentation and resuspension, (6) and degradation. The physical-chemical properties include density, vapor pressure, water solubility, environmental degradation rates, adsorbed/dissolved partitioning coefficients (K_{ow} , K_{oc}), viscosity, and surface tension. The chemical fates model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column and in the sediments. The model is three-dimensional, separately tracking surface slicks, entrained droplets or particles of pure chemical, chemical adsorbed to suspended particulates, and dissolved chemical. CHEMMAP may be run as a single scenario (forecast or hindcast) or in stochastic mode to estimate the probable distribution and concentrations resulting from wastewater discharges.

Select pharmaceutical and organic wastewater chemicals, contained in the Pharmaceuticals in the Environment, Information for Assessing Risk database maintained by the National Centers for Coastal Ocean Science, Center for Coastal Environmental Health and Biomolecular Research, are evaluated using CHEMMAP. Based on model outputs, it is possible to determine potential ecological hazards when discharged. The model results can then be used to indicate the volume of water that may be contaminated above toxicity thresholds provided in the Pharmaceuticals in the Environment, Information for Assessing Risk database.

Introduction

A wide variety of pharmaceuticals and other organic wastewater chemicals are continuously being discharged in our streams and rivers. It is important to understand how the water quality will be effected from such discharges, how far will the chemical be transported as well as what are the potential concentrations in the water.

In this study, we address the potential ecological hazards of two select pharmaceutical and organic wastewater chemicals. The discharge represents a hypothetical wastewater discharge containing active

ingredients in commonly prescribed antibiotics into a river. The hypothetical discharge is located along the Patuxent River in Maryland. ASA's chemical discharge model, CHEMMAP, was used to predict the fate of the antibiotics to identify the degree to which adverse impacts could occur to the environment. The specified chemicals are simulated to estimate maximum concentrations in water over time and dose. The chemical dose in the water column are compared to Ecological Structure Activity Relationships (ECOSAR) EC50 values for fish, algae, and daphnid.

CHEMMAP Model Description

The chemical spill model CHEMMAP has been developed over two decades for assessment of physical fate, biological impacts, natural resource damages and ecological and human health risks. While a few chemical spill models exist that can simulate transport and physical fate of single events (Lunel, 1991; Shen et al., 1995; Rusin et al., 1996), CHEMMAP is unique in being able to evaluate biological and human health impacts, and in its interconnection with hydrodynamic models, geographical information systems, and its graphical user interface. This makes the system flexible and applicable to marine and freshwater systems anywhere in the world. The algorithms and assumptions of the chemical spill model have been described previously (French et al. 1996, French McCay and Isaji, 2004; French McCay et al 2004). The fates model processes and database are briefly summarized below.

The chemical fates model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column and in the sediments. The model is three-dimensional, separately tracking surface floating chemical, entrained droplets or suspended particles of pure chemical, chemical adsorbed to suspended particulates, and dissolved chemical. Processes that are simulated are spreading (floating liquids), transport, dispersion, evaporation-volatilization, entrainment (liquids), dissolution, partitioning, sedimentation, and degradation.

The model uses physical-chemical properties to predict the fate of a chemical spill, including density, vapor pressure, water solubility, environmental degradation rates, adsorbed/dissolved partitioning coefficients (Kow, Kow), viscosity, and surface tension. The spilled mass is initialized at the location and depth of the release, in a state dependant upon the physical-chemical properties of the material. In the first hours to days after a spill, when acute effects to water column organisms would occur, the most important properties determining fate are density, vapor pressure, and water solubility. The adsorbed/dissolved partitioning coefficient (Koc), which is used in the model to compute the fraction dissolved versus adsorbed to suspended sediments, is functionally related and highly correlated with solubility. The value of Koc was calculated from Kow (which was obtained from literature compilations) using the regression equation from DiToro et al. (1991).

The spilled chemical is modeled using the Lagrangian approach, where multiple sublots, called spilletts, of the entire mass (or volume) spilled are tracked as they move in three-dimensional space over time (by addition of the transport vectors due to wind, currents, and buoyancy). The currents are tidal, provided by tidal chart vectors in a commercial (digital) tidal data program (Tides & Currents ®). Wind-driven current (drift) in the surface water layer (down to 5m) is calculated within the fates model, based on hourly wind speed and direction data (Youssef and Spaulding, 1993). Stoke's Law is used to compute the vertical velocity of pure chemical particles or suspended sediment with adsorbed chemical. If rise or settling velocity overcomes turbulent mixing, the particles are assumed to float or settle to the bottom. Settled particles may later resuspend (assumed to occur above 20 cm/sec current speed). Turbulent dispersion is modeled using a random walk scheme (Bear and Verruijt, 1987), with the magnitudes scaled by horizontal and vertical diffusion coefficients (Okubo, 1971). The vertical diffusion coefficient is computed as a function of wind speed in the wave-mixed layer, approximated as 1.5 times wave height, based on Thorpe (1984). Wave height is calculated using the algorithm outlined in CERC (1984).

Evaporation from slicks of floating chemicals is modeled following the approach in Mackay and Matsugu (1973) where the rate of mass flux to the atmosphere increases with vapor pressure, temperature, wind speed and surface area. Volatilization from the water column is calculated from the chemical's vapor pressure and solubility following the procedure outlined by Lyman et al. (1982). The mass flux to the atmosphere is transported in the air by the wind and degrades at an empirical rate estimated for in air (French et al., 1999, based on Mackay et al. 1992 b,c,d,e). The atmospheric dispersion model provided estimates of air concentrations in the air layer within 2 m of the water and land surface (i.e., within the approximate height of a person who might be exposed). The mass is dispersed horizontally by turbulence following the algorithm from Gifford (1961), as described in Csanady (1973). The model-calculated horizontal dispersion coefficient is a function of wind speed and air stability.

Chemical reactions are not specifically addressed in the model, i.e., the spilled mass is tracked through phase changes and transport, with all reaction products assumed to move together. Loss of chemical by reaction to some other form no longer of concern is included as degradation. Degradation is estimated assuming a constant rate of "decay" specific to the environment where the mass exists (i.e., atmosphere, water column or sediment). It may include biological, chemical or photochemical processes.

Chemical and Scenario Examined

Table 1 lists properties for the two selected active ingredients that are modeled along with their Chemical Abstract System (CAS) registry number, molecular formula, molecular weight, Log Kow, environmental half-life and ECOSAR EC50 for fish, algae and daphnid (NCCOS, 2006). The ECOSAR EC50 thresholds are model predicted concentrations that can be expected to cause a defined non-lethal effect in 50% of a given population, exposed for 96-hours (EPA, 2006).

A hypothetical discharge of chloramphenicol and sulfadiazine were simulated to estimate maximum concentrations in the water column over time and dose. The initial state assumed was pre-dissolved, since the scenario is simulating a wastewater discharge. A typical discharge rate of 100,000 m³/day with a concentration of 2 mg/L of selected active ingredient was assumed. The chemical was released 1 meter below the water surface. The length of the simulation was selected based on preliminary runs to determine the time of equilibrium and comparison of concentrations to the EC50 values.

Environmental and Other Input Data for Model Simulations

A geographical database defines water depth and shoreline type in the model. A grid covering the Patuxent River was prepared using World Vector Shoreline 1-100,000 dataset (U.S. Government MIL-W-89012). The cell size in the grid was 45m (W-E) by 70m (N-S). Gridded depth data, of the same dimensions, contained bathymetry from the Hydrographic Survey Data supplied on CD-ROM by the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Geophysical Data Center.

Currents have significant influence on the trajectory, and are important data inputs. Tidal currents were manually interpolated from tidal chart vectors in a commercial (digital) tidal data program (Tides & Currents ®). They are assumed rectilinear (in and out equal and opposite) and with two equal high tides per 25 hrs (M2). Downstream freshwater-driven river flow was not included.

The model uses an hourly wind time series specific to the time and location of the spill. This data is more influential to the fate of insoluble floating chemicals than contaminants in the water column. However, wind speed, duration and fetch are used to estimate wave height (CERC, 1984) and vertical dispersion in the surface mixed layer. Other environmental data inputs were assumed as follows, which are mean values for the Patuxent River salinity, 8 ppt; water temperature 20°C; suspended sediment concentration 10 mg/L.

The spill was assumed to represent of a wastewater treatment facility discharge that contains two chemicals that are active ingredients in a common antibiotic. The hypothetical treatment facility discharges into the Patuxent River located in Maryland. Table 2 lists the spill site latitude and longitude, along with other inputs defining the scenario, environmental conditions, and simulation parameters. For within-spillet concentration distributions, minimum horizontal and vertical diffusion coefficients over the potential range of values were assumed to provide conservative estimates of potential concentrations resulting from discharges.

Results

The model results indicate that both chemicals would disperse throughout the water column within a few hours after the discharge begins, and would reach a point of equilibrium two days after the initial discharge. The volume of water in which the dose exceeds the EC50 values for fish, algae and daphnid was determined (Table 3). The volumes in Table 3 are those in which there is the potential for non-lethal effects in 50% of a given population of fish, algae or daphnid. Table 4 displays the distance from the discharge location in which the concentration decreases below the EC50 value using a 96-hr exposure. Figures 1 and 2 show the maximum dissolved concentration resulting from the hypothetical discharge of chloramphenicol and sulfadiazine, respectively. Figures 3 and 4 show the area exceeding the EC50 value (calculated as dose for a 96-hr exposure) for fish, algae and daphnid for the chloramphenicol and sulfadiazine simulations, respectively. It should be noted that chloramphenicol concentrations do not exceed the EC50 values for fish, and sulfadiazine concentrations do not exceed the EC50 value for daphnid at any one time. However, when the dose is calculated for a 96 hour exposure duration, the EC50 values are exceeded.

Conclusions

This paper provides an analysis of two pharmaceutical and organic wastewater chemicals for a typical wastewater treatment facility discharging into a tidally driven river until equilibrium within the water column has been met. The modeling approach provides an objective, quantitative method for determining the environmental consequences of a discharge. The selected chemicals, chloramphenicol and sulfadiazine, evaluated in this paper demonstrate the ability to predict the effective distances and volume of water that could potential cause environmental impacts. It also demonstrates the importance when determining potential environmental effects that an analysis using dose should be done instead of concentrations at any one time.

This paper only investigates water column concentrations, an improvement would be to simulate the scenarios longer to examine potential sediment concentrations. An additional improvement would be to remove the bias of subjectively choosing the individual model runs to examine the consequence of the discharge. To do this one would have to perform stochastic modeling, which would provide a distribution of results with varying environmental parameters that may be statistically described. This type of approach would be important to understand the possible consequences that could occur with varied environmental conditions.

Table and Figures:

Table 1. Properties for selected pharmaceutical and organic wastewater chemicals (NCCOS, 2006).

Property	Chloramphenicol	Sulfadiazine
CAS Number	56-75-7	68-35-9
Formula	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₅	C ₁₀ H ₁₀ N ₄ O ₂ S
Molecular Weight	323.132	250.275
Log Kow	0.92	-0.34
Environmental Half-Life (days)	2.4 to 18.4	20-100
Solubility (mg/ml)	2.5	0.077
EC50 Fish (mg/L)	0.547	12.443
EC50 Algae (mg/L)	0.029	153.936
EC50 Daphnid (mg/L)	0.027	0.252

Table 2. Assumed model input parameters.

Name	Description	Value(s)
Spill Latitude	Latitude of the spill site	38° 30.76' N
Spill Longitude	Longitude of the spill site	76° 40.07' W
Discharge Rate	Rate chemical used to simulate discharge	100,000 m ³ /day
Discharge Concentration	Concentration used to simulate discharge	2 mg/L
Depth of release	Depth in water column released	1 m
Model time step	Time step used for model calculations	0.25 hour
Number of Lagrangian particles	Number of Lagrangian elements used to simulate discharged mass	1,000
Salinity	Surface water salinity	8 ppt
Temperature	Water temperature	20°C
Suspended sediment concentration	Average suspended sediment concentration during discharge period	10 mg/l
Horizontal turbulent diffusion coefficient	Randomized turbulent mixing parameter in x & y, for concentration distribution within a spilllet	1 m ² /sec
Vertical turbulent diffusion coefficient	Randomized turbulent mixing parameter in z, below the wave mixed layer	0.001 m ² /sec

Table 3. Water column volume (m³) where dose exceeds EC50 with 96-hr exposure.

Toxicity Threshold	Volume Exceeding EC50 (m ³)	
	Chloramphenicol	Sulfadiazine
EC50 Fish	4.46 x 10 ⁷	NA ¹
EC50 Algae	7.30 x 10 ⁷	NA ¹
EC50 Daphnid	7.35 x 10 ⁷	5.62 x 10 ⁷

¹ - concentration not reported in model predictions

Table 4. Distance (km) from discharge location where dose exceeds EC50 with 96-hr exposure.

Toxicity Threshold	Distance (km) from Discharge	
	Chloramphenicol	Sulfadiazine
EC50 Fish	3.75	NA ¹
EC50 Algae	4.9	NA ¹
EC50 Daphnid	5	4.5

¹ - concentration not reported in model predictions

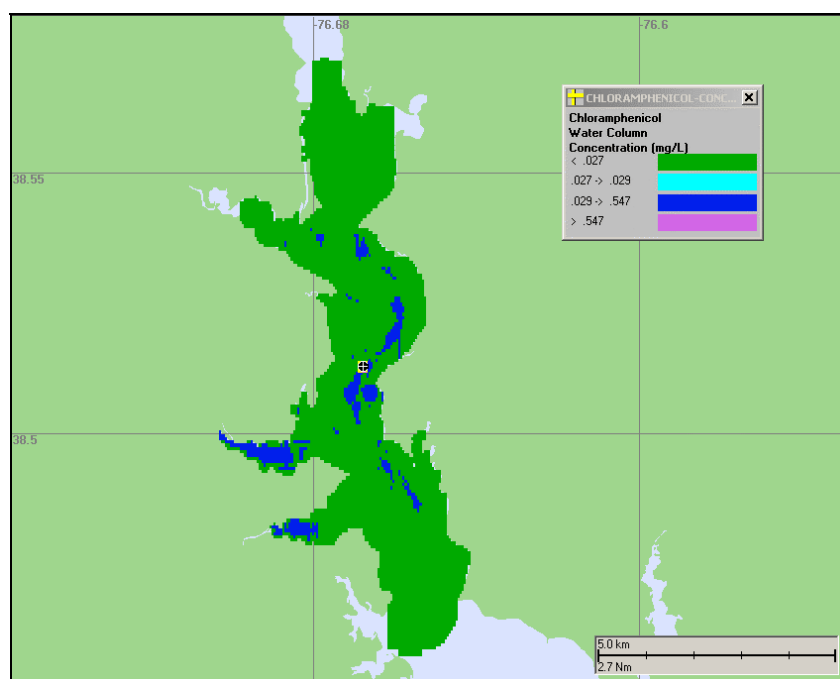


Figure 1. Aerial view of maximum dissolved concentration (mg/L) resulting from 100,000 m³/day discharge containing 2 mg/L of chloramphenicol. The map displays the highest vertically-averaged concentration at any time over 2 days.

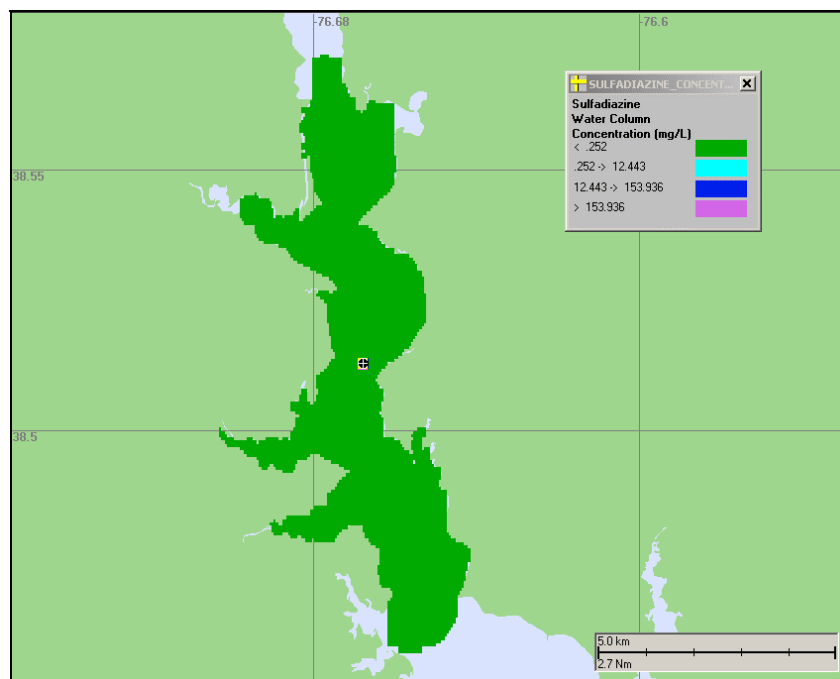


Figure 1. Aerial view of maximum dissolved concentration (mg/L) resulting from 100,000 m³/day discharge containing 2 mg/L of sulfadiazine. The map displays the highest vertically-averaged concentration at any time over 2 days.

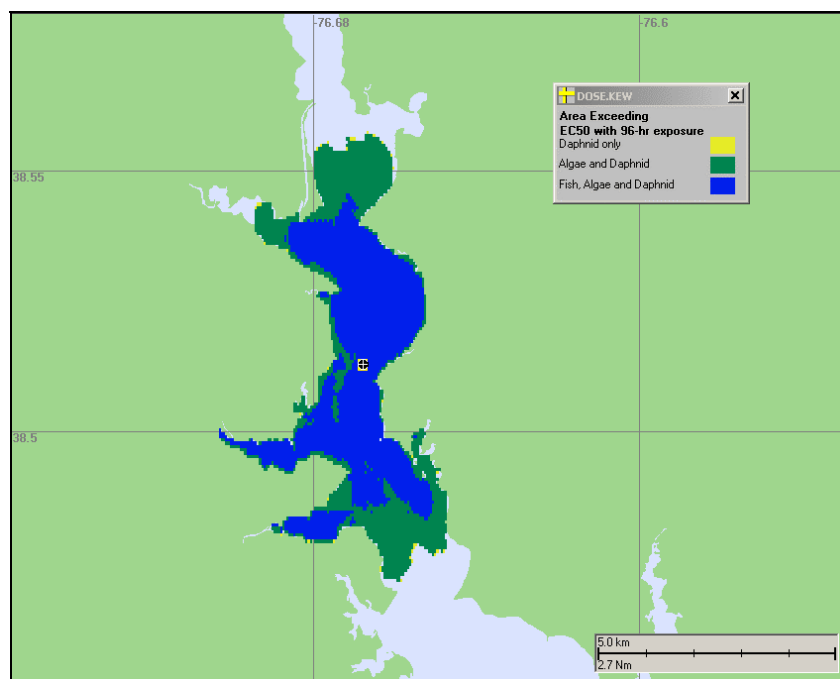


Figure 1. Aerial view of area exceeding EC50 value (calculated as dose for a 96-hr exposure) from 100,000 m³/day discharge containing 2 mg/L of chloramphenicol. The map displays the dose with an exposure time of 96 hours.

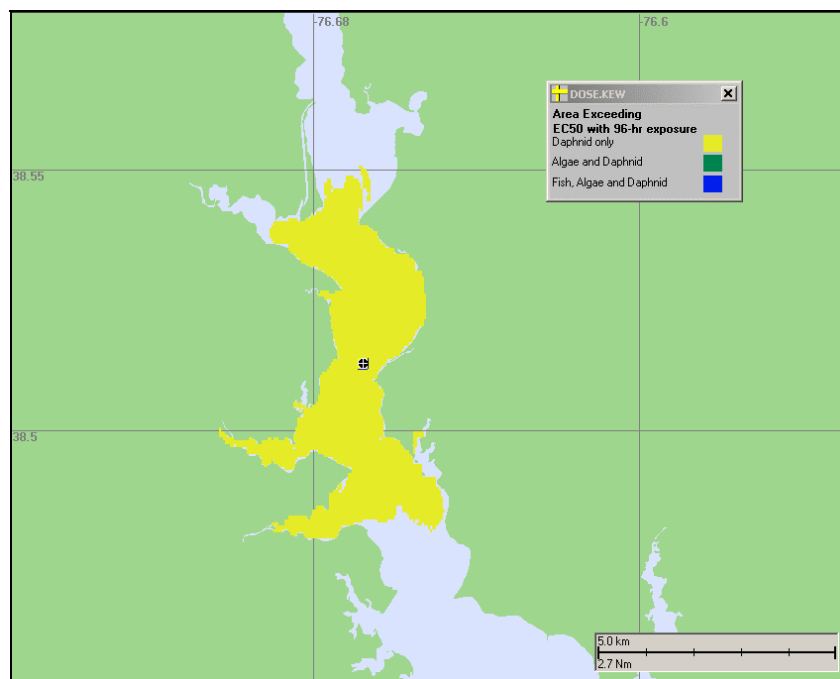


Figure 2. Aerial view of area exceeding EC50 value (calculated as dose for a 96-hr exposure) resulting from 100,000 m³/day discharge containing 2 mg/L of sulfadiazine. The map displays the dose with an exposure time of 96 hours.

References:

- Bear, J. and Verruijt, A. 1987. Modeling groundwater flow and pollution with computer programs for sample cases. Kluwer Academic Publishers.
- CERC, 1984. Shore protection manual, Vol. I. Coastal Engineering Research Center, Department of the Army, Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, MS.
- Csanady, G.T., 1973. Turbulent diffusion in the environment. D. Reidel Publishing Company, Dordrecht, Holland, 74p.
- DiToro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., Paquin, P.R., 1991. Annual Review: Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry* 10: 1541-1583.
- Environmental Protection Agency (EPA), 2006. Ecological Structure Activity Relationships. Available: <http://www.epa.gov/opptintr/newchems/tools/21ecosar.htm>
- French, D., Reed, M., Jayko, K., Feng, S., Rines, H., Pavignano, S., Isaji, T., Puckett, S., Keller, A., French III, F. W., Gifford, D., McCue, J., Brown, G., MacDonald, E., Quirk, J., Natzke, S., Bishop, R., Welsh, M., Phillips, M., Ingram, B.S., 1996. The CERCLA Type A Natural Resource Damage Assessment Model for Coastal and Marine Environments (NRDAM/CME), Technical Documentation, Vol. I -VI, Final Report, submitted to the Office of

Environmental Policy and Compliance, U.S. Dept. of the Interior, Washington, D.C., Contract No. 14-0001-91-C-11. April, 1996.

French, D., Schuttenberg, H., Isaji, T., 1999. Probabilities of oil exceeding thresholds of concern: examples from an evaluation for Florida Power and Light. In: Proceedings of the 22nd Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Environmental Protection Service, Environment Canada, pp.243-270.

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* 19(7-8): 629-644.

French McCay, D., N. Whittier, M. Ward, and C. Santos, 2004. Spill hazard evaluation for chemicals shipped in bulk using modeling. *Environmental Modelling & Software* 19: in press

Gifford, F.A., 1961. Use of routine meteorological observations for estimating atmospheric dispersion. *Nuclear Safety* 2:47

Lunel, T. 1991. Chemical spill model based on modeling turbulent mixing at sea. In: Proceedings of the Eighth Technical Seminar on Chemical Spills, Vancouver, BC, Canada, Environmental Protection Service, Environment Canada, pp.47-60.

Lyman, C.J., Reehl, W.F., Rosenblatt, D.H., 1982. *Handbook of Chemical Property Estimation Methods*. McGraw-Hill Book Co., New York.

Mackay, D., Matsugu, R.S., 1973. Evaporation rates of liquid hydrocarbon spills on land and water. *The Canadian Journal of Chemical Engineering* 51: 434-439.

Mackay, D., Shiu, W.Y., Ma, K.C., 1992a. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. I, Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*. Lewis Publishers, Chelsea, Michigan, 668p.

Mackay, D., Shiu, W.Y., Ma, K.C., 1992b. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. II, Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*. Lewis Publishers, Chelsea, Michigan, 566p.

Mackay, D., Shiu, W.Y., Ma, K.C., 1992c. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. III, Volatile Organic Chemicals*. Lewis Publishers, Chelsea, Michigan, 885p.

Mackay, D., Shiu, W.Y., Ma, K.C., 1992d. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume IV Oxygen, Nitrogen, and Sulfur Containing Compounds*. Lewis Publishers, Chelsea, Michigan, 930p.

National Centers for Coastal Ocean Science (NCCOS), Center for Coastal Environmental Health and Biomolecular Research, National Oceanic and Atmospheric Administration (NOAA), 2006. *Pharmaceuticals in the Environment, Information for Assessing Risk website*. Available: <http://www.chbr.noaa.gov/peiar/default.aspx>

Okubo, A., 1971. Oceanic diffusion diagrams. *Deep-Sea Research* 8:789-802.

Rusin J., Lunel T. and Davies L., 1996. Validation of the Eurospill chemical spill model. In: Proceedings of the 19th Arctic and Marine Oil Spill Program Technical Seminar, Calgary, Alberta, Canada, Environmental Protection Service, Environment Canada, pp. 1437-1478.

Shen, H.T., Yapa, P.D., and Zhang, B. (1995) `A simulation model for chemical spills in the upper St. Lawrence River,. J. Great Lakes Research 21(4) 652-664.

Thorpe S.A., 1984. On the determination of K in the near surface ocean from acoustic measurements of bubbles. Journal of American Meteorological Society 1984:861-863.

Youssef, M., Spaulding, M.L., 1993. Drift current under the action of wind and waves. In: Proceedings of the 16th Arctic and Marine Oil Spill Program Technical Seminar, Calgary, Alberta, Canada, Environmental Protection Service, Environment Canada, pp.587-615.