

## A COMPUTER MODEL FOR THE ATMOSPHERIC DISPERSION OF TOXIC VAPORS RESULTING FROM LIQUID CHEMICAL SPILLS

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### INTRODUCTION

In two previous papers, the authors presented results from computer models for downwind concentrations of toxic gases, resulting from continuous sources and from instantaneous releases (Dunn and Miller, 1979, 1981). A third case involving atmospheric dispersion of toxic gases can arise from the accidental spilling of a volatile liquid chemical and subsequent evaporation.

Chemical spills are an unavoidable risk in modern life. A popular news magazine (Huntley, 1983) reported an estimated 180 million shipments in the United States of explosive, corrosive, flammable, poisonous, or radioactive materials by highway, rail, water, and air each year. An atmospheric dispersion model for an evaporative spill is presented in this paper as well as the results obtained from a computer program developed for its application. This computer program should be very useful to local emergency planning committees formed as a result of the Emergency Planning and Community Right-to-Know Act of 1986. The program allows for a sophisticated and thorough analysis of problems arising from the accidental spillage of toxic liquids.

### DEVELOPMENT OF THE MODEL

The basic equation for downwind concentrations of toxic gases resulting from the evaporation of a liquid pool was obtained by considering the pool as a continuous source with zero plume height. This adaptation was applied to a standard model equation given for the prediction of downwind concentrations from a continuous source (Turner, 1970). The equation was further modified by doubling the concentration magnitude to allow for reflection by the ground surface. The resulting model equation is:

$$C = (2Q/\sigma_y\sigma_zU\pi)\text{Exp}[-.5(Y/\sigma_y)^2],$$

where  $C$  ( $\text{g}/\text{m}^3$ ) is the atmospheric concentration predicted for the specified position,  $Q$  ( $\text{g}/\text{s}$ ) is the emission rate or source strength from evaporation of the toxic chemical from the pool,  $\sigma_y$  (m) and  $\sigma_z$  (m) are the horizontal and vertical atmospheric dispersion coefficients,  $U$  (m/s) is the wind speed, and  $Y$  (m) is the lateral displacement from the centerline determined by the wind direction from the pool.

Data for the atmospheric dispersion coefficients are reported in the form of curve plots against downwind distance in families over the six weather stability

categories (Turner, 1970). These plots are on logarithmic scales varying over several orders of magnitude. Previously reported studies used functional approximations for these plots using logarithmic functions (Dunn and Miller, 1979, 1980). However, improved functional approximations using the exponential form ( $\sigma = ax^b + c$ ) to represent both  $\sigma_y$  and  $\sigma_z$  for  $x$  the downwind distance were developed for this project resulting in a simpler calculation that produced more uniformly accurate approximations. A relation was derived for the determination of the exponent  $b$  for three data points read from the curve plots. For  $\sigma_1, \sigma_2, \sigma_3$  obtained at distances  $x_1, x_2, x_3$  related by  $x_2 = kx_1, x_3 = kx_2 = k^2x_1$ , with  $k$  a numerical factor such as 4 or 10, it follows  $\sigma_1 = ax_1^b + c, \sigma_2 = ak^bx_1^b + c, \sigma_3 = ak^{2b}x_1^b + c$  and  $b = \log R_s / \log k$  for  $R_s = (\sigma_3 - \sigma_2) / (\sigma_2 - \sigma_1)$ . In some cases, solutions were obtained from several data sets and averaged. For  $\sigma_z$ , the distance range of  $1 \times 10^2$  to  $10^5$  m was divided into two subranges and separate solutions obtained on each. The final solution for the constants  $a$  and  $c$  were obtained by a modified linear regression which was derived to minimize the sum  $\sum_j [1 - (ay_j/\sigma_j) - (c/\sigma_j)]^2$ , for  $y_j = (x_j)^b, \sigma_j$  and  $x_j$  representing points taken from the curve plots. In this form the squared fractional or percent variations are minimized as suitable for data varying by orders of magnitude, rather than the more common squared magnitude variations, so that large and small values of the  $\sigma_j$ 's carry equal weight. Values computed from the functional approximations were found to agree in all cases to within five percent of values read from the curve plots.

Two literature reports were located which presented empirically established methods for the computation of evaporation rates from liquid pools exposed to wind currents (Clewell, 1983; Wade, 1942). Results from the two methods were found to differ appreciably but agree in order of magnitude. The evaporation rate given by Clewell (1983) with converted units is expressed as:

$$R = 2.222 \times 10^{-6} U^{.75} (1 + 4.3 \times 10^{-3} T^2) Z,$$

where  $R$  ( $\text{g}/\text{cm}^2\text{s}$ ) is the evaporation rate,  $U$  ( $\text{m}/\text{s}$ ) is the wind speed  $T$  ( $^\circ\text{C}$ ) is the pool temperature, and the factor  $Z$  is calculated as  $Z = P_v M / (P_H M_H)$ , for  $P_v$  ( $\text{mm Hg}$ ) and  $M$ , the vapor pressure and molecular mass of the specified chemical, respectively, and  $P_H$  and  $M_H$ , the vapor pressure and molecular mass of hydrazine, respectively. The evaporation rate given by Wade (1942) with converted units is expressed as:

$$R = 1.975 \times 10^{-9} M^{.71} P_v U^{.85},$$

with  $R, M,$  and  $P_v$  as before and  $U$  ( $\text{cm}/\text{s}$ ).

One set of experimentally measured values of evaporation rates of toluene at  $20^\circ\text{C}$  ( $68^\circ\text{F}$ ) at varying wind speeds had previously been obtained from a wind tunnel apparatus by a research student, Gary Lutz, at the University of Southern Indiana (Dunn, *et al.*, 1985). The wind tunnel apparatus, designed by the authors and constructed and donated by George Koch Sons Inc., was described in a paper presented by Charles Macer (Dunn, *et al.*, 1984). A comparison of results of both computations with these experimental results are given in Table 1, and it is seen that all agree in order of magnitude. Both the calculations of Wade (1942) and Clewell (1983) are employed in the model, with the larger value of the two selected for the atmospheric dispersion calculations. Since these calculations have rela-

TABLE 1. Comparison of computed and measured evaporation rates for toluene at 20°C (68°F) at various wind speeds. Rates are expressed as (g/cm<sup>2</sup>s) x 10<sup>4</sup>.

Wind Speed (mi/hr)	Computed Rate (Clewell)	Computed Rate (Wade)	Measured Rate (Lutz)
15.9	1.77	2.84	3.79
12.0	1.44	2.24	2.94
7.8	1.04	1.55	2.67
4.9	.73	1.04	2.00

tively high uncertainty, the worst case is selected to provide a factor of safety. The pool temperature is estimated as the ambient air temperature. The vapor pressure is calculated in the model for various chemicals from empirical formulas given in Lange's handbook (Dean, 1973). The emission rate to be used in the atmospheric dispersion model is calculated as the product of the evaporation rate and an estimated area of the pool.

The application of the model to the calculation of isopleths, curves of constant atmospheric concentration, is based on solving the previous atmospheric dispersion equation for the lateral displacement Y (m) at which a specified concentration occurs. The resulting equation is expressed as:

$$Y = \sigma_y [2 \text{Ln} (2Q/\sigma_y \sigma_z U \pi C)]^{.5},$$

in which Ln designates the natural logarithmic function and all the other symbols have the same meaning as before.

A computer program was written to carry out the computations of the model with various options. Provisions were made for entering the necessary parameters in common English units and converting them within the program to the metric units used in the calculations. The program initially reads in a data file containing the required data for specific chemicals. The data file contains the chemical name, the parameters required for the calculation of its vapor pressure as a function of temperature, the molecular mass, and the threshold limit value of concentration for safe exposure for each chemical. The file is in alphabetical order by the chemical name, so that after it is read into the computational program, the specific chemical can be searched out by name. An auxiliary program was written for preparation and augmentation of this data file. New chemicals and their data can be added to a previously prepared file and the file automatically realphabetized.

### APPLICATION OF THE MODEL

The evaporative spill computer model was written in BASIC for use on an IBM-PC equipped with a color graphics monitor. To use the full capabilities of the program, a printer and a Hewlett Packard model 7475A plotter are needed.

The person at the scene of the toxic liquid spill must input the name of the chemical, the estimated length and width of a rectangle that would encompass the pool, the ambient temperature, the wind speed, and the weather stability class. Once this information has been entered, the program responds with a menu listing the following three options: 1) downwind concentration at selected points;

TABLE 2. Downwind concentrations along the center line for an evaporative spill of benzene. Pool size 10 feet by 15 feet. Ambient temperature 80° F. Wind speed 5 mi/hr. Weather stability class D.

Downwind Distance (miles)	Concentration (mg/m <sup>3</sup> )	Concentration (ppm)
0.2	57.15	18.00
0.4	17.22	5.42
0.6	8.61	2.71
0.8	5.55	1.75
1.0	3.87	1.22
1.2	2.90	.91
1.4	2.28	.72
1.6	1.86	.59

2) downwind concentrations over incremented intervals; and 3) isopleth calculations with plot and display options.

**Downwind concentrations at selected points.** This option allows the rapid determination of the concentration of the vapors at any point downwind from the chemical spill. The point can be selected at any downwind distance either on or off the center line of the plume. This option would be useful if you knew of a sensitive area, for example, a school of a nursing home, at a given distance downwind from the spill, and you needed to make a rapid determination of whether or not a hazardous concentration of vapors might exist at that point.

**Downwind concentration over incremented intervals.** This menu selection allows the calculation of the downwind concentration of the vapors along the centerline at incremented downwind distances (Table 2). It also allows the computation of concentrations at downwind distances at a constant lateral distance from the center line. In addition, certain provisions allow the calculation of concentrations at incremented distances across the plume at a constant downwind distance.

The first two provisions in the program are useful in rapidly determining how far downwind a dangerous concentration of vapors would be expected. These values could be used to start an evacuation before the more precise evacuation area could be determined.

**Isopleth calculations with plot and display options.** Perhaps, the most useful aspect of the program is its capability to display evacuation zones on the screen or plot them on a graph. The screen option displays the evacuation zone on the computer monitor to an assigned scale. The plot command has two options: 1) plot to an assigned scale; or 2) plot to map coordinate scale (transverse Mercator). Option 1 allows you to plot an isopleth at a selected concentration. For example, if you selected 1 mg/m<sup>3</sup>, the program would draw an enclosed figure representing an evacuation zone as the total area encompassed by the 1 mg/m<sup>3</sup> isopleth. The plot would be drawn to any mapping scale that you select. Option 2 represents the most easily used plotting option. This option plots the evacuation zone to the scale of a geological survey map (Figure 1). The plot of the evacuation zone can be made on a transparency. The origin of the spill on the transparency

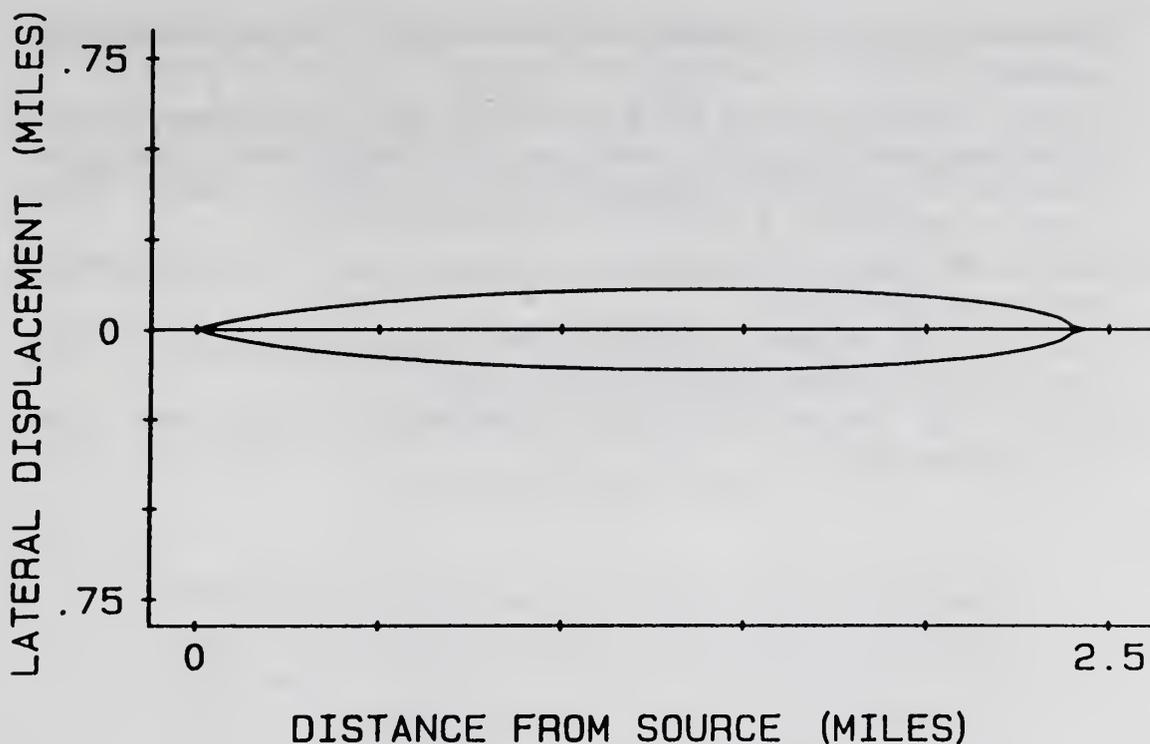


FIGURE 1. Isopleth for an evaporative spill of benzene. Pool size 10 feet by 15 feet. Ambient temperature 80° F. Wind speed 5 mi/hr. Weather stability class D. Isopleth concentration 1 mg/m<sup>3</sup>.

can be superimposed over the spill location on the geological survey map and the centerline on the transparency oriented to the downwind direction. The area for evacuation is immediately apparent.

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