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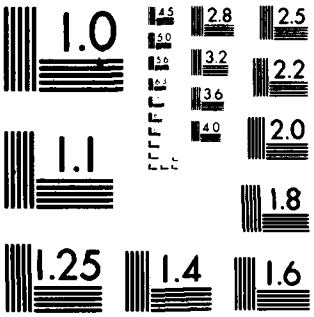

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MATHEMATICAL DEVELOPMENT OF THE SPILL ASSESSMENT MODEL (SAM) FOR HYDRAZINE AND SIMILAR ACTING MATERIALS IN WATER BODIES

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THE OBJECTIVE OF THIS WORK WAS TO DEVELOP A MATHEMATICAL MODEL FOR APPLICATION IN ASSESSING THE IMPACT OF CATASTROPHIC SPILLS. SPECIFICALLY, THE MODEL ADDRESSES INSTANTANEOUS AND CONTINUOUS POINT SOURCE DISCHARGES INTO WATER COURSES INCLUDING RIVERS, LAKES, AND ESTUARIES. THE SPILL MODEL PRIMARILY ASSESSES DISPERSIVE CHARACTERISTICS OF SPILLS OF THE HYDRAZINE FAMILY FUELS IN THE AQUATIC ENVIRONMENT; HOWEVER, THE DEVELOPMENT OF THE MODEL HAS BEEN → over

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CARRIED OUT IN A GENERALIZED FORM USING PARAMETERS AND INTERCHANGEABLE DATA ITEMS SO AS NOT TO RESTRICT THE SCOPE OF APPLICATION UNNECESSARILY. RESULTS WHICH CAN BE PRODUCED BY THE MODEL INCLUDE THE POLLUTANT CONCENTRATION AS A FUNCTION OF LOCATION, TIME, AND PHYSICAL, CHEMICAL, AND BIOLOGICAL CHARACTERISTICS OF THE POLLUTANT. THE SPILL MODEL ESTIMATES THE EXTENT AND DURATION OF HAZARDOUS CONCENTRATIONS IN WATER BODIES ASSOCIATED WITH ACCIDENTAL DISCHARGES AND DETERMINES WHEN THESE CONCENTRATIONS DROP BELOW TOXIC LEVELS. THE SPILL MODEL IS DESIGNED TO BECOME A MANAGEMENT TOOL TO SUPPORT A CLEAN-UP OPERATION IN THE EVENT OF A SPILL, TO PROVIDE EMERGENCY DISCHARGE CONTINGENCY PLANNING, TO PERMIT POST-INCIDENT ANALYSES, AND TO SERVE AS A BASIS FOR FURTHER DEVELOPMENT OF METHODS OF HAZARD ASSESSMENT.

PREFACE

This report was prepared by Arthur D. Little, Inc., Acorn Park, Cambridge, Massachusetts 02140 under Contract F08635-79-C-0084 with the Air Force Engineering and Services Center (AFESC), Tyndall Air Force Base, Florida 32403. Captain George W. Schlossnagle was Project Engineer for AFESC.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). It will be available at NTIS to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

1. OVERVIEW

Current U.S. Air Force operations dictate the use of numerous toxic substances, and among these are the three hydrazine family fuels (anhydrous, unsymmetrical dimethyl, and monomethyl hydrazine). Hydrazine fuels are the basic rocket propellent for strategic missiles and satellites, and the joint NASA- and USAF-sponsored Space Shuttle Program will greatly increase the volume of hydrazine in general use. Bulk storage and transport of hydrazine fuels could lead to accidental discharges, and if a discharge finds its way into a water body, undesirable consequences could occur to the aquatic ecosystem. The objective of the work described in this report was to undertake the development of a mathematical model for application in assessing the impact of catastrophic spills.

Specifically, the spill model addresses instantaneous point source discharges into water courses including rivers, lakes, streams, and estuaries. The primary requirement of the spill model is to assess dispersive characteristics of spills of the hydrazine family fuels in the aquatic environment; however, the development of the model has been carried out in a generalized form using parameters and interchangeable data items so as to not unnecessarily restrict the scope of application. Results which can be produced by the model include the pollutant concentration as a function of location, time, and physical, chemical and biological characteristics of the pollutant. A spill model of this type estimates the extent and duration of hazardous concentrations in water bodies associated with accidental discharges, and when these concentrations drop below toxic levels. Such a model could become a management tool to support a clean-up operation in the event of a spill, to provide for emergency discharge contingency planning, permit post-incident analyses, and serve as a basis for further development of methods of hazard assessment.

Previous analytical and computer modeling approaches provided the basis and foundation from which the further development of the water dispersion model for use with the hydrazine family fuels was undertaken. The spill model computes the concentration of a water-miscible liquid or solid at any specified point and given time for a discharge on the surface of a lake, river, or estuary. All the chemical discharged or spilled is assumed to go into solution with water. The same model can also be used for the dispersion of insoluble solids which are neutrally buoyant or whose settling times are large compared to mixing times. The model can also be used approximately for concentration estimates for those liquids which react with water or whose boiling point is less than that of ambient temperature. This report describes the analytical formulation of the model, a majority of the assumptions explicitly or implicitly made, details the derivations used to arrive at the form of the model equations, and discusses methods of using the models to develop hazard estimates.

The remaining subsections of the introduction address topics that are fundamental to the formulation of the model. The characteristics and potential hazards of hydrazine fuels are described, and chemical and physical properties are given. The overall framework and approach for hazard estimation embodied in the CHRIS and HACS systems is described to provide background for the context within which development of earlier versions of the water dispersion model occurred. The final two subsections of the introduction describe the types of spill environments incorporated in the model, introduce coordinate systems and related spatial geometries, and detail the behavior of the different types of discharge or release conditions. The body of the report then addresses the development of the models to estimate the extent and duration of the spreading of the chemical substance introduced into the aquatic environment by these discharges.

The phenomenon of mixing is described by the classical diffusion equations with one or more diffusion or dispersion coefficients. Solutions of the diffusion equation for different types of receiving water bodies and assumed release or discharge conditions result in different mathematical models for estimating the dispersion of a spilled chemical over time and distance. However, the characteristics of these different solutions have many similarities, and the more complex behavior in receiving water bodies of three dimensions can be approached by first considering elementary solutions for diffusion in one dimension.

Section II of the report first discusses the form of the generalized diffusion equation in three dimensions, and then uses the equation in one dimension to develop methods of solution for different types of release conditions. As each solution is derived, additional characteristics of the fundamental concentration distributions are described. At the end of this section, the methods of generalizing from these solutions to three-dimensions is introduced.

In Sections III, IV, and V the different models for the waterborne dispersion of a miscible substance are presented. Each section deals with the models appropriate for the particular receiving water body: still water or lakes, nontidal rivers, and tidal rivers. The sections are organized in order by increasing complexity of the dispersion process, as modeled by solutions of the classical diffusion equation, so that additional modeling complexities are introduced as they occur. Within each section, the different types of models appropriate for different types of release or conditions in the receiving water body are developed. Each section concludes with a summary of the model equations, required input data, and computed results.

2. CHARACTERISTICS AND HAZARDS OF HYDRAZINE FUELS

The characteristics and hazards of hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH) are described in terms of their physical and chemical properties. In addition, an overview is given of available methods for assessing environmental effects of these chemicals, with primary emphasis upon interactions within an aquatic medium.

a. Basic Properties

Table 1 summarizes the basic physical and chemical properties of the three materials. Additional information for hydrazine include:

- Hydrazine is a miscible liquid, is a mildly alkaline base, and has approximately the same density as water.
- Hydrazine is quite hygroscopic and tends to absorb water, carbon dioxide, and oxygen from the atmosphere.
- The vapors of hydrazine may ignite spontaneously with air or oxygen.
- Hydrazine and water form a maximum boiling azeotrope so that water as an impurity in hydrazine causes a lower vapor pressure than would be the case for the pure liquid.
- Hydrazine is a powerful reducing agent. Reactions with strong oxidizing agents may cause violent uncontrolled deflagration.

Additional data for unsymmetrical 1,1-dimethylhydrazine (UDMH) include:

- UDMH is hygroscopic and somewhat unique in that it is completely miscible in both polar and nonpolar solvents.

TABLE 1. HYDRAZINE FUEL PROPERTIES

	HYDRAZINE	1,1-DIMETHYLHYDRAZINE (UDMH)	MONOMETHYLHYDRAZINE (MMH)
Formula	N_2H_4	$(CH_3)_2N-NH_2$	CH_3NHNH_2
Molecular Weight	32.05	60.11	46.07
Boiling point (°C)	113.5	63.3	87.5
Freezing point (°C)	1.5	-57	-52.4
Specific gravity (at 20°C)	1.008	0.791	0.878
Vapor pressure at 20°C (mm Hg)	14.4	156.8	49.6
Heat of vaporization (Cal/g)	299	145	209
Heat of solution (Cal/g)	-121	-10 (est)	?
Viscosity of liquid (centipoise)	0.913	0.492	0.775
Flash point (°F)			
Open Cup	100	--	62
Closed Cup	--	34	--
Flammable limits in air (Vol %)	4.7-100	2-95	2.5-98
Odor	Ammonia-like odor	Fishy or Ammonia-like odor	Ammonia-like odor
Solubility in water	Miscible	Miscible	Miscible

- UDMH can be classified as a weak base and a strong reductant having antioxidant properties.

Additional points of interest for monomethylhydrazine (MMH) are:

- MMH is less reactive than hydrazine but readily undergoes reactions with a variety of organic and inorganic compounds.
- Like hydrazine, MMH is a strong reducing agency, weakly alkaline, miscible, and very hygroscopic. It reacts with carbon dioxide and oxygen in air.

b. Fire and Explosion Hazards

All three substances of interest are flammable in air and may ignite spontaneously in the presence of oxidizing materials. Hydrazine, for example, may ignite when exposed to large surface areas such as rags, cotton waste, and sawdust[1].

Dilution with water reduces the flammability of any of these substances. At concentrations below 40 percent in water, a hydrazine solution cannot be ignited. At a 50-percent concentration, ignition will occur only if the solution is heated to a temperature near its boiling point[1].

If ignition does occur involving a quantity of UDMH, it cannot be assumed that the products of combustion are harmless. Under certain conditions, it has been shown that the poisonous gas, hydrogen cyanide,may be formed in concentrations as high as 1.5 percent in air[1].

In the liquid form, hydrazine, MMH, and UDMH cannot simply be exploded by stock, friction, or electric discharge. A variety of initiating mechanisms, however, can lead to explosive decomposition of their vapors[1].

c. Toxicity to Humans

All of these substances are toxic to the extent that prolonged exposure to high concentrations in air or ingestion of sizeable doses can be lethal. Sublethal effects of the vapor include dizziness, nausea, chest pain, coughing, wheezing, and/or hoarseness appearing gradually over long exposure periods[2].

Exposure of the eyes to vapor can cause itching, swelling of the mucous membranes, painful blistering, and burns similar to those caused by a welding arc. In all cases, the symptoms will depend upon the concentration and duration of exposure, as well as the resistance of the individual[2].

Ingestion or skin contact with absorption may cause caustic burns, headache, dizziness, nausea, or even death, depending upon the nature of the exposure. In this respect, hydrazine tends to cause surface burns whereas UDMH tends to cause internal effects due to absorption through the skin. Hydrazine is considered by some to be up to 15 times more toxic than UDMH when in contact with the body, or up to 3 times more toxic when ingested. UDMH and MMH tend to be most dangerous by inhalation of vapors[1].

All three of the substances of interest are suspected of causing cancer in man, based on demonstration of carcinogenesis in one or more animal species by appropriate methods[3,4]. The American Conference of Governmental Industrial Hygienists[3] has adopted Threshold Limit Values-Time Weighted Averages (TLV-TWA) for airborne concentrations for hydrazine of 0.1 ppm, for UDMH and for MMH of 0.2 ppm. The time weighted average concentration is for a normal 8-hour workday or 40-hour workweek to which nearly all workers may be repeatedly exposed without adverse effect.

- As with many toxic substances, however, occasional higher exposures for short time periods may be tolerated with little or no ill effects. Dogs subjected to the vapors of UDMH have withstood 1 hour exposures to 50 ppm, 200 ppm for 15 minutes, and

600 ppm for 5 minutes with no observable adverse effects[1], and NIOSH has estimated[5] that UDMH vapor concentrations below 50 ppm are not immediately dangerous to life and health for one half hour human exposures in emergency situations. Similar limits for hydrazine and MMH are 80 ppm and 5 ppm, respectively. (The latter value, appearing somewhat out of context, is based on experimental observations with laboratory mice, MMH having been shown most toxic in animal experiments.)

- The National Institute for Occupational Safety and Health (NIOSH) has recommended[4] limits for hydrazine, UDMH and MMH of 0.03, 0.06, and 0.04 ppm respectively for chronic exposures.

d. Toxicity to Aquatic Organisms

Toxicity to aquatic organisms has not been studied to an extent that allows a complete description of effects. Nevertheless, available data may be useful in assessing the potential damage to eco-systems from spills of hydrazine and its derivatives into water.

Table 2 summarizes results[6] of experiments sponsored by the U.S. Air Force at the Irvine Campus of the University of California and involving the growth of algal systems in varying types of water bodies. These are mostly useful for demonstrating the order of magnitude of concentrations that are safe or harmful.

In simulated spill situations with experiments involving stickleback fish[6], it was found that 50 percent of the fish expired within 96 hours when the initial concentration of hydrazine in water was 6.6 ppm. During this time period the hydrazine concentration dropped by approximately 50 percent of initial values as assessed by actual measurements.

TABLE 2. TOXICITY TO ALGAL SYSTEMS[6]

Water body Characteristics	HYDRAZINE		UDMH		MMH	
	SC*	EC_{50}**	SC	EC_{50}	SC	EC_{50}
Freshwater-oligotrophic conditions, 3-day exposure	0.001	0.02	0.5	0.08	--	--
Freshwater-intermediate nutrient status, 3-day exposure	0.001	0.013	0.5	4.7	--	--
Freshwater-eutrophic, 3-day exposure	0.001	0.006	0.5	5.3	--	--
Seawater-full salinity w/inshore coastal nutrient level, 6-day exposure	0.0005	0.0008	--	--	--	--
Seawater-full salinity w/nutrients as in estaurine waters, 6-day exposure	0.001	0.0011	0.01	0.92	0.2	0.5

*SC = safe concentration in parts per million (ppm); i.e., concentration at which growth was not inhibited.

**EC_{50} = concentration (ppm) at which growth is 50 percent inhibited.

-- = data not reported.

Other aquatic organisms (aufwuchs) were found to be more sensitive to hydrazine, with 50 percent expiring within 96 hours at an initial concentration of 3.2 ppm of hydrazine in water.

e. Environmental Degradation of UDMH

Hydrazine, UDMH, and MMH will slowly decompose when released into the air or water and will form a variety of decomposition products. A study[7] of UDMH decomposition in water serves to demonstrate the speed of this process and its possible consequences.

The study found that:

- The decomposition reaction is inhibited by the presence of acid in the water.
- Trace metal ions in the water tend to have a catalytic (i.e., accelerating) effect on the reaction.
- Microbes in the water may help degrade certain products of the decomposition reaction.

Among the possible decomposition products that were mentioned are formic acid, ammonia, dimethylamine, dimethylnitrosamine, diazomethane, nitrous oxide, methane, carbon dioxide, formaldehyde, the short-lived 1,1-dimethyl-diazene, tetrazene, and others that are as yet unidentified. The number and variety of products, as well as their respective toxicities and the factors that regulate their formation, all lead to the observation that it is difficult to properly judge the potential effects of a UDMH spill into the environment. Although the UDMH decomposes, it forms products which are themselves possibly harmful. The same statement also generally holds true for hydrazine and MMH.

In lake water experiments[7], the half-lives of the disappearance of UDMH was determined as a function of pH at a temperature of 30°C. The results were:

pH	$t_{1/2}$ (hours)
5	630
6	66
7	10
8	4.5
9	3.9

Given knowledge of the pH of a water body and assuming first order decay for which $\exp(-kt) = C/C_o$, one can compute the value of the first-order decay coefficient from the expression:

$$k\ (\mathrm{min}^{-1}) = \frac{1.155 \times 10^{-2}}{t_{1/2}} \qquad (1)$$

where $t_{1/2}$ is the half-life (in hours), corresponding to the given pH value. Similar data, unfortunately, do not appear to be available for hydrazine or MMH, although results mentioned previously of the stickleback fish experiments do provide some crude guidance for hydrazine.

f. Action of Hydrazine and Its Derivatives Upon Release

From this overview of the properties and characterisitics of these substances, it is possible to develop profiles of their expected actions upon release to the environment. Since spills into water are of primary concern, it is assumed that the liquids find their way into a body of water and do not first become ignited. Nevertheless, comprehensive assessments of spill hazards should fully consider the significant probability of early ignition and/or detonation.

Development of a water-spill profile for hydrazine requires special consideration of the facts that:

- The density of hydrazine is between that of pure water and sea water, and the substance is fully miscible. It will mix with water as rapidly as would a cup of coffee spilled into a lake, river, or estuary.
- Hydrazine's heat of solution is a significant fraction of its heat of vaporization. Indeed, for every 2.5 grams that dissolve into water, sufficient heat is generated to vaporize a gram of pure hydrazine.
- The freezing point of hydrazine is 1.5°C (34.7°F). It may form a solid on the ground or in water quite rapidly in very cold weather; the solid would dissolve in water.
- The vapors of hydrazine are quite toxic. Although concentrations as high as 80 ppm can probably be tolerated for half hour exposures in an emergency, with no significant adverse effects, the possible carcinogenicity of the substance, and the impact of this finding in the minds of the public, suggest that vapor exposures should be minimized to the greatest extent possible. Similarly, concern must be given to possible ingestion of water supplies or aquatic organisms that have been contaminated by hydrazine. A previous discussion has focused on the potentially lethal effects of hydrazine on fish and algal systems.
- Hydrazine will decompose in water to form a variety of reaction products, many of which may also be harmful. Limited data[6] suggest a half-life in bay water of 80 to 100 hours or thereabouts for hydrazine itself.

Overall, one would expect a hydrazine spill into water to be generally characterized by rapid mixing of the substance with water; evolution of some amount of vapor at the spill site, and to a lesser extent, from the surface of the body of water entered; and dispersal of the contaminant throughout the water body with potentially adverse effects upon fish and other aquatic wildlife until concentrations of hydrazine and its decomposition products drop below safe limits.

Important characteristics for UDMH include the observations that:

- UDMH is fully miscible with water and about 20 percent less dense than water. Although it will have an initial tendency to float on the surface of a water body, it will also mix readily if any sort of turbulence is present. An analogy would be the ease with which alcohol mixes with water.
- The heat of solution of UDMH is estimated to be only a small fraction of that of hydrazine. Nevertheless, the fact that its vapor pressure is 10.9 times that of hydrazine at 20°C (68°F) suggests that vapor evolution could be a significantly greater problem with UDMH.
- UDMH is also a suspected carcinogen. Although half-hour vapor exposures to 50 ppm are likely to be tolerated with little or no effect, it will be necessary to actively ensure that exposure of the public is minimized. Similarly, risks of exposure by ingestion must be addressed. Previous discussion has focussed on the effects of UDMH on algal systems. Fish and other aquatic organisms

are also likely to be adversely affected.

- The flash point and lower flammability limit of UDMH are relatively low. Under appropriate conditions, there is a possibility that vapors from the spill site or body of water can travel downwind and become ignited, or enter an enclosed space and explode.

Overall, the actions of UDMH would generally be similar to those of hydrazine. However, UDMH would mix somewhat more slowly with water, would evolve a greater volume of vapors, and would present significantly greater flammability hazards as well as toxicity hazards.

The properties of MMH place its expected actions between those of hydrazine and UDMH. It is less dense than hydrazine but more dense than UDMH. Similarly, its vapor pressure at 20°C (68°F) is 3.4 times that of hydrazine, but roughly one-third that of UDMH; MMH has a flash point and lower flammability limit that are, respectively, lower than hydrazine's but higher than UDMH's. Like the other two substances, it also is a suspected carcinogen. Although concentrations of up to 5 ppm can probably be tolerated for one-half hour without major ill effect, inhalation and ingestion exposures should be minimized to the greatest extent possible.

g. Water Dispersion Models

This report presents a number of models that allow the user to estimate the concentration of a contaminant in water as a function of spatial position and elapsed time from initiation of discharge. Addressing both instantaneous and continuous releases into lakes, non-tidal rivers, and estuaries, the models can be useful tools for contingency planning and/or assessment of the adverse effects of a spill.

There are various attributes of the water dispersion models that merit discussion. These essentially involve limitations on the capabilities of the models in representing the specific actions of hydrazine, UDMH, and MMH upon release to an aquatic environment. Major topics of interest include model formulation assumptions of mass conservation, neutral buoyancy, and water body configuration, among others.

All of the models allow for depletion of the contaminant in water through first-order decomposition reactions. Available data for UDMH in particular allow estimation of the necessary decay coefficient (k) as a function of pH. There are two serious problems, however, in using this attribute of the models to full advantage. The first stems from the observation that analogous data do not appear to be available for hydrazine and MMH. The second from the clear indication that one or more of the decomposition products of any of the three substances of interest are likely to be highly toxic or otherwise harmful to the environment themselves.

An associated problem, which is mostly important for UDMH, somewhat less so for MMH, and least important for hydrazine, involves the fact that none of the water dispersion models available currently have the capability to estimate the amount or rate of vapor evolution from the surface of a contaminated water body. Since vapor evolution depletes the amount of contaminant in solution, this inability leads to a certain degree of conservatism in predictions of concentration.

A suggested solution to the first problem of mass conservation is to ignore the decomposition reactions by setting the decay coefficient for each subject material to zero. Although this approach may provide conservative concentration predictions for the spilled pollutant in water, it serves to better account for the possible adverse effects of decomposition products. The second problem of vapor evolution simply cannot be solved at this time with any of the available models.

All of the models additionally assume that the spilled pollutant has the same density as water, i.e., is neutrally buoyant. For hydrazine, the assumption is perfectly acceptable. For UDMH and MMH, since these substances are somewhat lighter than water, the assumption can affect the accuracy of predictions under certain conditions. The adverse effect should not be highly significant, however, since the difference in density is not great, and both substances are fully miscible in water.

Further limitations in model formulation stem from the manner in which the models address the configuration of the affected water body. Each of them generally assumes some set of typical water body characteristics, even though real world bodies of water are far from being uniformly similar. Overall, therefore, it is seen that any concentration predictions provided by a model are simply best estimates consistent with current knowledge of dispersion phenomena.

(1) Other Hazard Assessment Models

Within the Chemical Hazards Response Information System (CHRIS)[2,8,9,10,11] of the U.S. Coast Guard are a number of components that can be of assistance in assessing the adverse impact of spills of hydrazine and its derivatives. Among these are included the Hazard Assessment Handbook (CG-446-3) and the Hazard Assessment Computer System (HACS). Each contains a variety of models addressing such phenomena as vapor dispersion, vapor evolution, and pool fires, among others. Previously developed models appropriate for use with the hydrazine fuels are briefly identified:

Model P in these components is the primary water dispersion model and forms the basis of the models presented in this report. It allows users to very rapidly assess the impact of a spill upon downstream water users under emergency conditions, as well as for contingency planning purposes. In consequence, there is a potential for vulnerable downstream resources to not only be warned of a spill, but to be provided with specific time of arrival, duration, and concentration estimates. Limitations of the model are essentially a function of the assumptions with which it is formulated, and variations in solubility, density, reactivity, and/or volatility are not presently included.

Model R is useful for instantaneous spills of miscible liquids which have high vapor pressures at ambient temperatures. For still waters and non-tidal rivers, it utilizes the mixing and dilution equations of the water dispersion model to estimate downstream concentrations on the surface of a water body, and from these, the vaporization rate of the contaminant at each point. Integration of these vaporization rates over an appropriate surface area of the water body provides a crude estimate of the total amount of vapor liberated, and this estimate can then be used for approximate assessments of subsequent vapor dispersion hazards. A significant limitation of the current version of this model is that it does not attempt to adjust the concentrations in water to account for the amount of previously vaporized contaminant.

Model C in each component is a vapor dispersion model allowing estimation of contaminant concentrations in air. Although it is difficult to apply to the case of a moving source of vapors (contaminant flowing downstream in a river, for example), its use can provide an upper bound to the downwind areas that may be subjected to excessive vapor concentrations.

The pool burning Model E predicts the distances from a fire that are safe for buildings and people. Mostly applicable for spills of insoluble, floating substances on water, and spills of any type of flammable liquid on land, it can also be roughly applied to spills of hydrazine and its derivatives onto water.

It should be noted that each of these models addresses specific phenomena which chemicals can display on release. When a specific chemical discharge displays a multiple set of phenomena, it is appropriate to utilize all models of pertinence and to utilize judgment in the interpretation of results. Additionally, each model contains tradeoffs between the degree of its accuracy and the nature of the input data required. None are necessarily as complex as could be formulated, but all can be utilized with a basic set of input data usually readily available or reasonably estimated for any given water body and spill situation. Requirements for extensive input data pertinent only to a local environment have been minimized wherever possible.

3. FRAMEWORK FOR HAZARD ASSESSMENT

Accidents involving the discharge of chemicals on water may cause hazards, the consequences of which may result in loss of life, limb, natural resources, and/or property. A chemical discharge or spill on water can create a hazard because of its flammability, its toxicity, or both. As the spill disperses and becomes diluted, the hazard normally decreases and disappears. If knowledge can be obtained of how far and how fast a spilled chemical may spread, the hazards can be assessed in terms of the distance and time over which the spreading chemical may be toxic, hazardous, or flammable.

The processes of dispersion, evaporation, combustion, and the like, which are associated with spills of chemicals on water, are quite complex and depend on many variables, including the nature of the chemical itself, conditions of the accident or spill, environmental conditions at the time and place of the spill, and the nature of the interaction of the spilled chemical with the aquatic environment. As a consequence, comprehensive assessments of the extent of hazards produced by an accidental discharge require identifying and describing the different types of chemical behavior on release, their interactions and their contribution to different types of hazards. The Chemical Hazard Response Information[9], known as CHRIS, and the Hazard Assessment Computer System[11] component of CHRIS, known as HACS, which have been developed for the U.S. Coast Guard, provide a systematic, simplified approach to identifying the appropriate processes governing a given chemical release and methods for estimating the hazard. Basic hazard estimates can be obtained in terms of distances over which a toxic or flammable concentration of a given chemical may exist and the minimum safe distance between the spill site and people, combustible materials or protected resources.

One of the spill models originally formulated for use within HACS and CHRIS addressed the prediction of hazards caused by the accidental spill of a toxic chemical miscible with water on different types of receiving water bodies. When a miscible chemical is spilled on the water surface, it rapidly mixes with the water. This mixing is primarily caused by flow non-uniformities (turbulence) or in some cases by wave action. Because of the predominance of certain types of phenomena in different regions of the different types of receiving water bodies, the model for water dispersion of miscible substances is actually composed of a series of different theoretical predictive methods. This serves the purpose of estimating the concentration levels of the dispersing chemical in water at different locations and different times after the occurrence of a spill at some point.

Since the objective of the work described in this report was the further development and refinement of the spill model for the dispersion of miscible substances in water, it is important to recognize and emphasize that the model describes a particular type of chemical behavior and the consequences of that behavior. Additional hazards may result from other behavior on release; therefore, in this section the overall framework for hazard assessment provided by CHRIS and HACS is introduced and the approach and concepts employed in these systems are beiefly described.

a. Overview

CHRIS and HACS were designed to enable quick and accurate estimates of hazards presented by a discharge, or potential discharge, of hazardous chemicals, and to provide these estimates in a form useful to response personnel. The broader scope of CHRIS encompasses a compendium of chemical data, data on response methods, data bases for contingency plans, and field manuals, in addition to analytical methods and manual procedures for quickly obtaining hazard estimates. HACS was originally developed as an extension of the analytical procedures included in CHRIS to extend the level of detail and accuracy beyond that possible for simplified field procedures.

HACS is a computer-based system, incorporating the mathematical models originally developed as the basis for the field calculation procedures implemented in CHRIS, and a number of specialized models developed specifically for computer application. The design and implementation of HACS focussed on providing rapid and quantitative assessments in response to questions such as the following:

- When will the air/water concentration of a discharged material reach a specified level of toxicity at a given location?
- When will the air/water concentration return to a specified safe or nontoxic level?
- What is the concentration of discharged material at a specified location and time?

Both CHRIS and HACS are generalized systems, encompassing different types of chemical behavior and different types of hazards. They have been designed for use under emergency conditions involving the actual or potential accidental discharge of a hazardous material into navigable waters and for such non-emergency uses as contingency planning (pre-planned assessments and responses), training, and evaluation and improvement of assessment methods.

b. Information and Use Requirements

The evaluation of a hazard due to a chemical discharge was considered to involve the following sequence of action:

- Determination of information pertinent to the on-scene conditions at the spill site.
- Selection of appropriate calculation procedures.
- Evaluation of the extent of hazards as indicated by these calculations.

Within CHRIS, information describing on-scene conditions was considered to fall in two categories: (1) that which is absolutely essential for even the most basic assessment of hazard potential and (2) that which will permit a more refined and accurate assessment if time permits. For use with HACS, a broader class of information inputs were postulated, encompassing on-scene data, characteristics of chemical behavior that might be independently obtained, and computer system parameters for use in selecting tables and graphic displays of hazardous conditions. Provisions were then included within HACS to permit computations to be carried out under the realistic condition in which not all desired information is available.

The types of information relating to the discharge conditions at the scene of the spill as incorporated in HACS are:

- Discharged chemical characteristics (e.g., name, storage pressure, temperature, quantity).
- Discharge conditions (e.g., tank size, location of discharge opening relative to water's surface and to tank level).
- Environmental conditions (e.g., wind speed, air and water temperatures).
- Marine conditions (e.g., current speed, water depth at spill site, spill geography).

c. Specification and Selection of Calculation Procedures

Once the chemical being discharged has been identified, the hazard presented can be assessed provided the nature of the interactions of the chemical with water is known. The approach utilized for CHRIS and HACS was to classify the different types of water interactions that might occur and then to list chemicals of interest into these interaction categories. Since the chemical behavior depends on a variety of factors, including chemical properties and environmental conditions, chemicals grouped by one type of interaction may also separately and individually be associated with other types of interactions, and multiple types of hazard situations may be presented as a consequence of the release of a specific substance.

The resulting classification approach was developed in the form of a hazard assessment tree and is represented by Figure 1. Given the properties of the discharged chemical and ambient conditions, the appropriate vertical path in the tree can be selected and followed to determine which calculation procedures should be used for the particular chemical.

The first box (beneath ACCIDENT) in Figure 1 is designated by the letter A and represents a quantitative description of the discharge, e.g., the chemical, its rate of flow or total quantity discharged, the state of the discharged chemical, and significant parameters, such as temperature and pressure. Depending on the state of the released chemical (gas, liquid, solid, or mixture), it can be said to belong to one or more of the vertical paths represented in Figure 1:

- Gases
- Liquids
  - Non-reacting with water
    - Boiling point below ambient temperature of water
    - Boiling point above ambient temperature of water
  - Reactive with water
  - Self-reacting (polymerization, decomposition, etc.)
- Solids
  - Soluble
  - Insoluble
  - Reactive.

Along each path flowing from the release condition in Figure 1 are decision points that are based upon physical properties and environmental conditions. Following these decision points are a series of calculation procedures

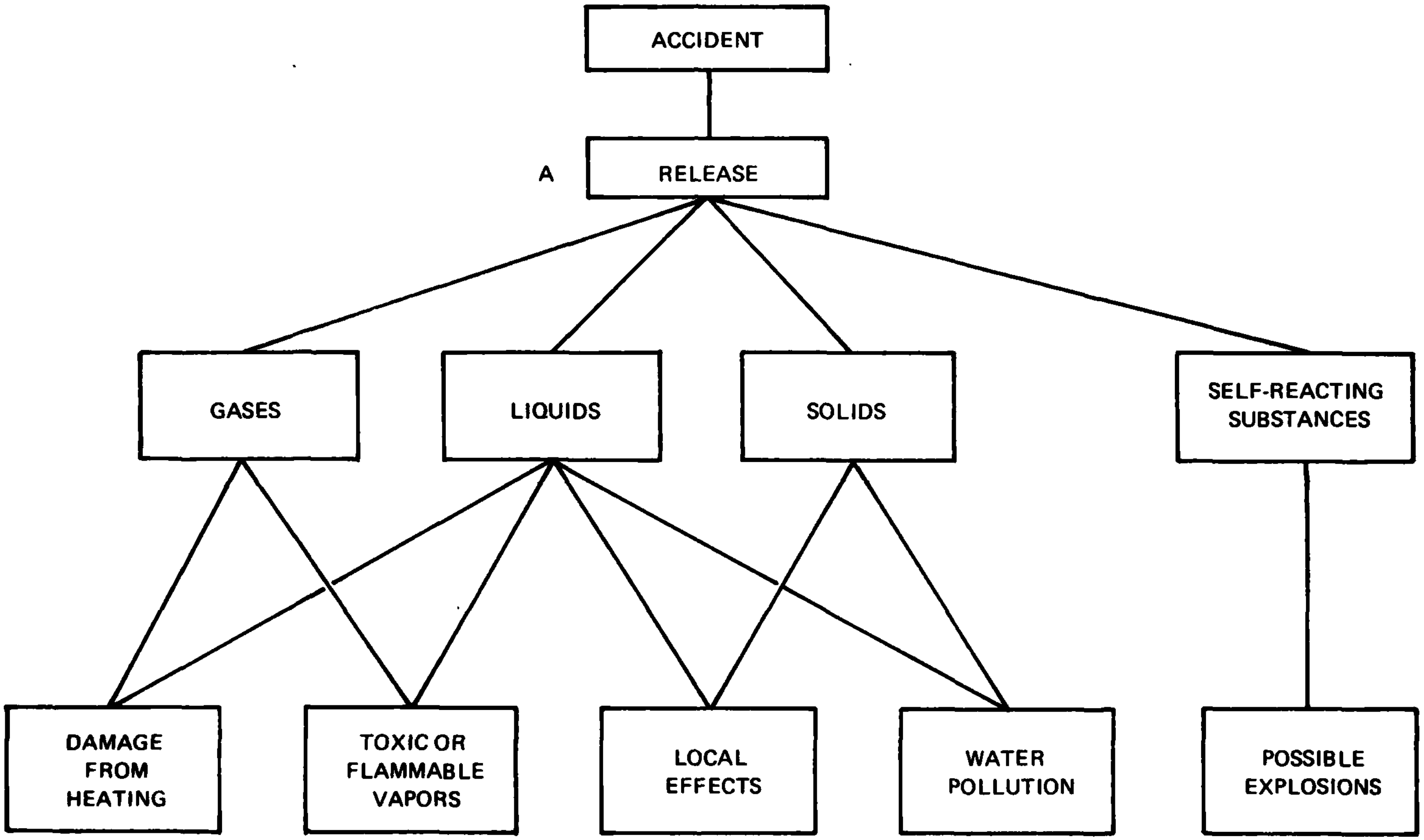


Figure 1. Discharge Hazards

which mathematically represent different physical phenomena (boiling, dispersion, etc.). While these procedures simply indicate how rapidly certain physical processes are taking place, they are essential because they help determine the extent of the hazard. Each calculation procedure is designated by a letter, so that a particular path may be referred to by a series of letters. This series of letters is called the "hazard assessment code" and is identified in CHRIS and HACS for each chemical considered; currently data is contained on 900 compounds. Each path eventually leads to one or more points of hazard evaluation. By indicating which calculations must be performed and providing generalized methods of making the desired calculations, CHRIS and HACS allow one to progress along the appropriate path and determine the potential hazard presented by a chemical discharge.

Each branch (or path) of the tree represents a particular assessment estimation route which describes the behavior of a particular type of chemical under a given set of user specified accident conditions. Since the properties of a chemical may vary with ambient conditions (i.e., temperature), and in some cases, depending upon the chemical spilled, various types of hazards are possible for a given set of accident conditions (e.g., gas or liquid release), some chemicals may follow more than one route down the tree. These alternatives have been reflected in the hazard assessment codes given in CHRIS and HACS. Each scenario or possible situation for which an assessment may be desired makes up a subset of the total hazard assessment code given. At present, HACS accepts only one subset of these alternatives (defining a single branch) at a time, producing the hazard assessment for that subset. It is important that the user recognize that a number of computer runs (one for each possible subset) may be required to fully assess all the hazards which may be presented by the spill of a given chemical under particular conditions.

d. Hazard Assessment

Once the identity of the discharged chemical and the associated hazard assessment code have been established, the appropriate hazard assessment calculation procedures can be carried out.

Within CHRIS, the hazard assessment is made manually with simplified calculations utilizing graphs and tables. Corresponding to each letter in the hazard assessment code is a calculation procedure displayed in graphic or tabular form. Some procedures are generalized and can apply to several chemicals whereas others are specific for an individual chemical.

In HACS, however, the calculation procedures are embodied in a set of specific computer programs for estimating discharge conditions and chemical behavior. Each program contains one or more mathematical models[12,13] for the calculation procedures along the hazard assessment tree, and the individual models contained within HACS are also identified by similar one or two letter codes. In the present configuration, those models applicable to discharges of the hydrazine fuels include: (A) release or discharge model; (P) concentration of water-miscible liquid or solid for a discharge into a lake, river, or estuary; (Q) pool fire model for soluble liquids which have a boiling point greater than ambient; (R) for vapor evolution from a chemical discharge into water; and (S) for vapor dispersion in support of model R. The work described in this report addressed the refinement and enhancement of the model for the concentration of a miscible chemical in water (P).

HACS provides estimates of hazards in the following manner: The system first begins by accepting user input which provides identification of the chemical substance which was spilled, discharge conditions, marine conditions, and environmental conditions.

To obtain detailed chemical specific properties, the current models automatically interface with a separate data base containing information on 900 chemicals. Since this file contains only the quantitative data required to operate the simulation models, it is a subset of the chemical data given in CHRIS. Each chemical is identified by a 3-letter code which is entered by the user to retrieve the desired physical property data. The codes for the hydrazine fuels are: (DMH) unsymmetrical dimethyl hydrazine; (HDZ) hydrazine; and (MHZ) methylhydrazine. Physical properties for these chemicals are recorded as data constants or empirical functions of temperature.

Some properties, not measured in the laboratory, have been estimated using techniques which have been proven acceptably valid for similar chemicals. The techniques were selected and utilized by R. Reid, co-author of the standard reference, "The Properties of Gases and Liquids" by Sherwood and Reid[14, 15,16]. Properties are arranged in alphabetical order by chemical code (the three-letter recognition code assigned to each chemical) and all properties pertaining to a given chemical are contained in one logical record, automatically available to HACS for conducting a hazard assessment.

Since not all items used in the file apply to each chemical, a data quality or type scheme is used. Each data item in the file, for each chemical, has a code assigned with it to indicate whether the value entered is exact, an estimate, or not applicable. The properties for a given chemical are accessed by specifying the recognition code for the desired chemical. This is the only input required by the user to obtain the required physical and chemical properties associated with the discharged chemical. However, the data type scheme provides a means for allowing data entered by the user to override values that would otherwise be selected from the property file. Thus more accurate chemical data, if available, can readily be substituted, or effects of variations in physical properties can be investigated.

If HACS requires additional data that has not been provided by the user or obtained from the chemical properties file, the system automatically retrieves nominal values from an internal default file. The default file is used to (a) define the characteristics and units of measure of all input items and computed results and (b) provide reasonable estimates or default values for each item to enable hazard assessments to be made under conditions of limited data availability.

Overall control of the input operations is provided by the user input processor portion of the HACS system which accepts and stores user input data in optional systems of measure, provides limit tests for the reasonability of input data and estimated computed hazard levels, coordinates the internal use of data and computed values according to a data item quality hierarchy, and provides overall control of the assessment computation sequence (for example, allowing single runs, or iterative computations for sensitivity analyses). This portion of the system also contains all generalized software used for producing output reports and plotted displays of model outputs.

On completion of the input processing step, HACS begins the estimation or assessment calculations. This process is the execution of a sequence of mathematical models, specified by the user according to a path of the hazard assessment tree, to obtain information such as the concentration of the discharged material at a specified location and time after the onset of a spill.

If flow rates are known, or if other information (such as pool diameters) that normally would be calculated by HACS models is available from field observations, the execution of assessment models may be selectively omitted by submitting user inputs to override (i.e., replace) information which would otherwise be calculated by the model. HACS contains an internal data priority or hierarchy scheme which provides decision logic to permit the user to override values which would otherwise be calculated as model outputs. This capability also allows the user the option of not omitting the execution of a particular model while at the same time overriding all or part of the output of the model which might normally be passed as input to a subsequent model. In this event, HACS will execute the model for which overriding output values have been provided, display the calculated results, and then substitute the override values for use as may be required in subsequent calculations. This enables the user to compare calculated results with information available from independent sources or on-scene observations and to make qualitative assessments of the relative reasonability or accuracy of these values.

When the execution of the models specified for a particular hazard assessment scenario has been completed, the system produces textual reports, and, if desired, optional tables and/or plotted output displays. The system output identifies the spilled chemical, restates the discharge, environmental and marine conditions, and reports the hazard assessment. The output enables the user to validate input data quickly and accurately. The system can plot thermal radiation, concentration, or other variables (e.g., pool radius, temperature of liquid remaining, and volume of liquid remaining) as a function of location and/or time, as appropriate. The objectives of the system are to obtain and display estimates of the dispersion of a chemical or the effects of that dispersion in the environment as a function of distance and time in terms of the extent to which flammable or toxic limits may be exceeded. The subjective interpretation of the potential hazards as a consequence is not included within the scope of the system.

The development of HACS has proceeded through several evolutionary stages, initially encompassing the encoding of the analytical models developed for use with CHRIS, then continuing through the development of extended computer simulation models, internal file structures, and output display capabilities. The existing version of HACS has been placed in operation by the U.S. Coast Guard, and at the present time further development of the system is being focussed on two areas. First, the basic assessment models are being refined to reflect advances in modeling techniques and the needs of users requiring information in real world situations. Second, the development of a fully interactive terminal interface for HACS has been initiated to provide a dialog, by means of remote terminal, between the user and the system as the operations of input and calculation proceed. This interface is being developed under the control of, and integrated with, the internal default data definition and priority scheme to enable the system to automatically guide users through the input requirements, selectively display prompts, and respond to user direction during a calculation sequence.

4. TYPES OF SPILL ENVIRONMENTS

When a water miscible liquid is spilled on a water surface, mixing takes place, thereby diluting the liquid. The mixing is caused by molecular diffusion in calm water and mass convection (turbulent diffusion) in streams, rivers, estuaries, and the sea. Mixing may take place preferentially in one direction, depending on the flow conditions, flow geometry, water density gradients, and the like. Because of the predominance of certain types of mixing phenomena in different regions of the navigational waters, the spill environments are broadly classified as: lakes, non-tidal rivers, tidal rivers, estuaries or salinity intrusion regions of tidal rivers, and open sea[12].

In non-tidal rivers the main agency for mixing is stream turbulence. In tidal rivers, estuaries, and also in the open sea, wave action becomes quite important in addition to the stream or current velocity. In estuaries and other regions where a density stratification of water due to salinity is likely to be found, mixing caused by the density-driven circulation can become extremely important. However, since the velocities involved in these circulations are small and the area influenced by these flows is generally large, only long-time effects are important. For assessing the hazards caused by a relatively infrequent spill (even though the tonnage of the spill itself may be large) the effects of salinity-driven mixing can be ignored[12].

In later sections of this report, detailed descriptions are given of the nature of the turbulent dispersion processes predominating in these different regions, methods available for describing these processes and the feasibility for inclusion in a generalized spill model of this type. For some cases, such as large lakes and regions of the open sea, quantitative descriptions requiring data unique to a specific spill location are not readily available for use in a generalized model.

In general, the receiving water bodies are treated as three-dimensional non-isotropic volumes, that is, turbulent dispersion is assumed to occur at different rates along the principal coordinate axes selected for the water body. Where appropriate, applicable methods for obtaining or computing values of these dispersion coefficients are presented, and, where necessary, simplifying assumptions are suggested and incorporated in the computerized version of the model. However, the form of the theoretical expressions as implemented continue to reflect the non-isotropic nature of the dispersion processes, so that different values of the turbulent dispersion coefficients can readily be used in place of internally computed values should suitable alternate generalized methods of computation become available.

The predominant types of receiving water bodies then are distinguished for the purpose of modeling by the predominant nature of the motion of the water body:

- Still Water - in which different dispersion currents may occur in different directions, but the water body is characterized by the absence of bulk motion of the receiving fluid (thus the reference to still water). Also, as implemented the geometry presently incorporated for the still water case assumes that the boundaries of the water body are located far from the location of the spill so that unconfined dispersion occurs in three directions. The model therefore is only strictly appropriate for spills occurring in large lakes, or regions of open sea, far from shore, and in the absence of significant wind, wave action, or induced currents.
- Non-Tidal Rivers - in which the characteristics of the water body are non-isotropic, with turbulent dispersion occurring at different rates in different directions, and where bulk fluid motion of the receiving water body occurs in one direction (downstream) at a uniform rate. In many cases the influence of turbulent diffusion in the longitudinal direction is commonly considered to be negligible with respect to the bulk fluid motion. Also, in addition, the river cross section is assumed to be bounded by channel banks

and bottom so that the lateral spread of the chemical in the water may be confined. The longitudinal (downstream) direction is assumed to be unbounded.

- Tidal Rivers - in which the same configuration is assumed as for a non-tidal river with the addition of a sinusoidal tidal velocity component superimposed on the non-tidal river velocity.

a. Water Body Coordinates and Geometry

(1) Still Water

The coordinate system used for spills into still water (lakes and open sea) is shown in Figure 2. The origin of the coordinate system is at a point on the surface of the water body, the x and y axes lie in the plane of the water surface and the positive z-axis is downward so as to form a right-handed orthogonal coordinate system. Since the dispersion is unconfined, the region of potential interest is given by all values of x and y, and values of $z \geq 0$ (for depth).

The origin of the coordinate system is taken at the location of the spill so that the coordinates of a point in the still water system also specify position relative to the spill. This is not the case for river system coordinates.

(2) River System Coordinates

Figure 3 identifies the coordinate system (x,y,z) used for spills into both non-tidal and tidal rivers and illustrates the assumed river channel geometry. The river channel is assumed to be rectangular in cross-section, having a constant width w and a constant depth d. The origin of the river coordinate system is taken at the centerline of the river on the surface. The half-width of the river, the distance from the centerline to either bank,

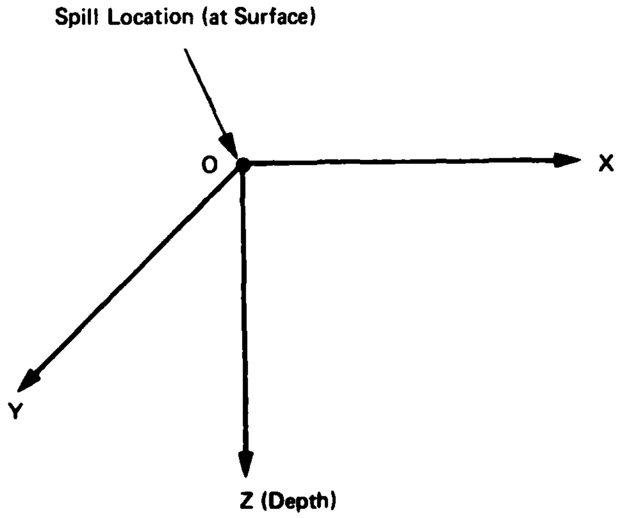
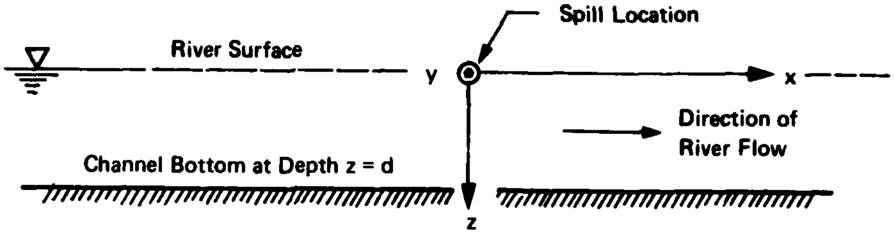
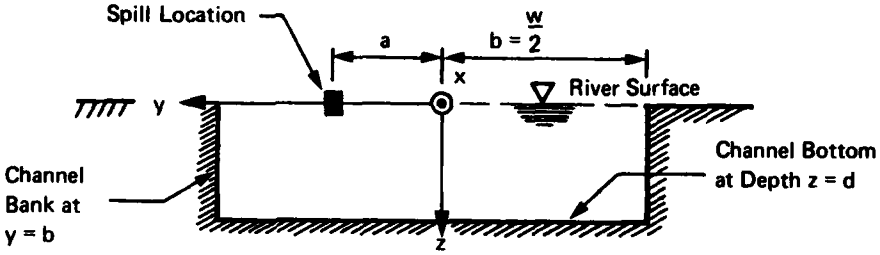


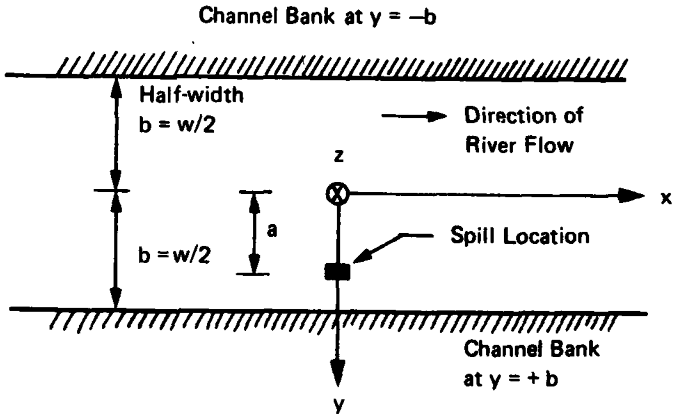
Figure 2. Still Water Coordinates



(a) Longitudinal Section of River



(b) Lateral Section of River



(c) Plan View

Figure 3. **River System Coordinates**

is denoted as b. In river system coordinates, the positive x axis gives downstream distance, positive z gives depth below the surface, and y is cross-stream so as to form a right-handed coordinate system.

For non-tidal rivers, the bulk fluid motion is assumed to occur in the x-direction, at a constant uniform cross-sectional velocity given as u. For tidal rivers, an additional sinusoidal tidal velocity is superimposed on the non-tidal velocity.

The location of a spill in a river is taken to be at the surface ($x = 0$, $z = 0$) at a point in the channel offset from the centerline by a distance given as a. Positive values of the offset a correspond to spill locations in the positive y direction. Since the coordinates of any position in the river, given in river coordinates, do not also specify position relative to the spill location (unless $a = 0$), a transformation is required for the general case of spills occurring at offsets from the centerline.

b. Observation Point Coordinates

In this context the observation point refers to the location (time and distance) in the coordinate system of the receiving water body at which the concentrations resulting from a spill of a chemical are to be obtained. Although occasionally absolute time may be used in the body of this report to substantiate or clarify derivations, the time at which the concentration at the observation point is desired is always specified by the elapsed time from the start of the spill.

(1) Transformation from Spill Coordinates to Water Body Coordinates

Solutions of the governing diffusion equation express the concentration of a spilled chemical in terms of the distance from the spill location and generally in terms of elapsed time from the start of the spill.

For still water, since the origin of the coordinate system is taken at the spill location, the coordinates of an observation point relative to both the water body system and the spill are identical, and the still water coordinates (x,y,z) may be directly substituted for the corresponding spatial coordinates in the diffusion equation solutions.

For river system coordinates, solutions of the diffusion equation express concentrations in the receiving water body, in general, in the form $c(\alpha,\beta,\gamma,t)$ where the origin of the spatial coordinates (α,β,γ) is taken at the spill location on the surface of the river. The direction of the coordinate axes are assumed such that the positive α-axis is along the downstream direction, the positive γ-axis is downward, and the positive β-axis is cross-current so as to form a right-handed coordinate system. The form $c(x,y,z,t)$ expresses concentrations in the river with reference to a fixed point in the river geometry, while $c(\alpha,\beta,\gamma,t)$ expresses the concentration with respect to the spill origin in the water moving with the current.

Application of this equation to spills into rivers of rectangular cross-section first requires a transformation from the spill-centered coordinates α, β, γ to the river system coordinates x, y, z which reference the spill location to the channel geometry. Second, the concentrations expressed in spill coordinates as $c(\alpha,\beta,\gamma,t)$ usually represent unconstrained flow, that is, concentrations of the pollutant are given for values of the coordinates α, β, γ increasing without limit, and it is necessary to impose constraints arising from the boundary conditions, for flow in rivers, at the channel surface, banks, and bottom. The method of applying these constraints is described in the section on the non-tidal river model.

The transformation between the spill-centered coordinates (α,β,γ) and the river system coordinates is obtained from the definition of the river system coordinates as:

$$\begin{aligned} x &= \alpha & \qquad & & \alpha &= x \\ y &= a + \beta & & \text{or,} & \beta &= y - a \\ z &= \gamma & & & \gamma &= z \end{aligned} \tag{2}$$

Thus, solutions obtained from the diffusion equation relative to spill-centered coordinates in the form $c(\alpha,\beta,\gamma,t)$ are transformed to concentrations relative to river system coordinates by simple substitution yielding $c(x,y-a,z,t)$.

c. Coordinate Constraints

For spills in still water, the coordinates (x,y) of an observation point may be positive or negative, while the z coordinate (depth) must be greater than zero. Values of elapsed time less than zero should yield concentrations of zero at all locations. Although x, y, z, and t may take on large values, limits should exist beyond which computed concentrations should be zero; the values of these upper limits will, in general, depend on the behavior of the dispersing chemical.

Since the river system geometry is more complex, additional constraints are required. The location of the spill must be contained within the river channel:

$$-b \le a \le b \tag{3}$$

Symmetry could be used to restrict the allowed values of the offset, a, to only positive values of y; however, this is not necessary. The y coordinate of the observation point must also similarly be constrained to lie within the channel banks:

$$-b \leq y \leq b \tag{4}$$

The observation point must be located at or below the surface, but at or above the channel bottom:

$$0 \leq z \leq d \tag{5}$$

The coordinate of the observation point in the longitudinal direction, x, will have upper and lower limits depending on the behavior of the dispersing chemical and the type of model used. In some cases, at very short times after the start of a spill, some concentrations may occur for small negative values of x. As for spills in still water, both x and t may take on large positive values, but should also have finite upper limits beyond which only zero values of concentration can be obtained to within available numerical accuracy. For values of elapsed time less than zero, concentrations at all locations should also be zero.

The dimensions of the river channel, the half-width b (or the width w), and the depth d must be greater than zero. Depending on the specific formulation of the river models, it may also be necessary to constrain the bulk fluid flow such that the velocity u is non-zero; however, some river solutions of interest may degenerate without difficulty to still water models.

(1) Confined or Unconfined Dispersion

For the lake or still water model, the spill is assumed to occur in a region of water far from shore so that the effects of the shore or bottom in confining the spread of a chemical in water may be neglected. In the case of spills in non-tidal rivers, however, the channel banks or bottom may act to restrict the dispersion of the chemical and give rise to different regimes or sub-environments for inclusion in the models.

For the initial stages of a spill into a non-tidal river, at a point on the surface of the water sufficiently far removed from either bank, the spread of the chemical will occur in a nearly unconfined manner (such that the effects of the channel banks may be neglected). During the initial stages of unconfined dispersion, the spill model utilizes a three-dimensional formulation of the dispersion equations to obtain values of the concentration at any point in the river cross-section; this form of the concentration equation is commonly referred to as a near-field model, and applied for times close to the start of the spill when the effects of channel confinement are negligible.

Depending on the relative depth and width of the river, and the location of the spill point with respect to the channel geometry, at some time after the start of a spill, the effects of the channel boundaries become more significant and the mixing will tend to become more or less uniform in either the horizontal direction, the vertical direction, or both. At some later time, complete mixing across the cross-section of the river can be assumed, and a simplified model, based on this assumption, can be used to obtain the cross-sectional average concentration. Such a model is referred to as a far-field approximation, or one-dimensional model, since the average concentration is assumed to be a function only of time and longitudinal distance from the spill point. The primary advantages of such a model are that the computations are significantly simplified for regions far removed from the spill point, and analytical approximations for very large times and distances are readily developed.

For the intermediate region of interest, between the near-field and far-field extremes, a two-dimensional model could be postulated based on uniform, or nearly uniform cross-sectional mixing in one cross-sectional direction but not the other, with appropriate boundary conditions specified to govern the limits of applicability of the model. However, the effects of the channel banks and bottom may also be directly incorporated in the three-dimensional or near-field model by a method of superimposing contributions from virtual spill sources to satisfy the boundary conditions at the channel limits. This is the method that has been utilized for the spill model so a separate two-dimensional spill model is not required. In fact, if a sufficiently large number of virtual sources were included, the near-field model could also be used for large times or distances in place of the far-field model.

Details of the application of virtual sources and the specification of the transition between the near-field and far-field models are presented in the section describing non-tidal rivers.

5. TYPES OF CHEMICAL RELEASE

The dispersion of a chemical in water is affected by the initial conditions at the start of the release and whether the discharge takes place over an extended duration. Releases are characterized as point sources or distributed sources to indicate the initial spatial distribution of the released chemical. Relatively simple mathematical expressions are readily obtained for point sources in which a finite amount of chemical substance is initially introduced into an infinitesimally small volume of the receiving water body; these models have a disadvantage in that the estimated concentration at the spill location has an infinite value initially and will exceed the density of the spilled chemical for some time after the start of the spill. Distributed sources, on the other hand, refer to releases which take place over a finite dimension, which may be a line (1-D), area (2-D), volume (3-D), or any combination of these. In a later section of this report the effect of the initial source distribution on the resulting concentration profiles is illustrated. The second fundamental characteristic of the spill process is whether the spill of the entire amount of substance occurs instantaneously, or continuously over some finite duration. Commonly, continuous spills are assumed to take place over long durations, and the initial rise time as the dispersing chemical spreads through the receiving water body is usually neglected. Thus, most solutions obtained for continuous spill conditions represent steady-state concentration distributions where, subject to the conditions of the start and cessation of a release of finite duration, the steady-state concentration at any observation point x, y, z is independent of time. The third subject considered here is the nature of the chemical degradation or decay process which may take place as the spilled chemical is dispersed in the receiving water body. Although this behavior is not, strictly, a condition of the chemical release, the governing continuity (or mass balance) partial differential equation can readily be transformed to obtain concentrations in terms of a fixed rate constant and an initial amount of spilled chemical. Also, applications based on the principle of conservation of mass are simplified if the total mass of a chemical dispersing in the environment, as a function of time (but not distance), can be expressed in terms of the initial chemical release.

a. The Instantaneous Point Source

[Text of the following six paragraphs appearing in brackets was abstracted from a discussion given in reference[17] pertaining to dispersion in air; although the context has been modified for the purpose of this report, much of the concept and text have remained unchanged.]

[The instantaneous point source is the conventional approximation to the type of release associated with a very short venting of material, such as might be associated with an explosion, tank car derailment or similar occurrences of short duration. The term instantaneous point is a mathematical simplification since even a small, rapid explosion will have finite time and space dimensions. The slug, or mass of spilled chemical, once formed, moves away from the source with a speed and direction determined by the prevailing bulk *fluid velocity of the receiving* water body (as in the case of a river).] In still water the mass of the spilled chemical remains centered about the spill location (only turbulent dispersion or molecular diffusion takes place and this simplified behavior is not discussed further).

[The mean speed and direction of the slug can be expected to change from the original values during its travel as the pattern of river currents in which it is embedded changes with time.] Since specification of river current variations is not practical within the objectives of a generalized spill model, a limiting assumption is employed that the river flows with a constant cross-sectional velocity so that the center of mass of the spilled slug moves downstream, along a longitudinal line from the spill location, at a constant rate equal to the river velocity.

[As the slug moves, it will expand about its center owing to the action of turbulent fluctuations. If an idealized slug is embedded in a uniform turbulent field in which all the turbulent elements are smaller than the dimensions of the slug, the entire mass of spilled chemical will be carried downstream in a uniform manner. The slug will grow in size as its edges are mixed with the water by turbulence. This growth is accompanied by a proportional decrease in concentrations within the slug.]

[If the slug is originally embedded in a field of turbulent elements that are considerably larger, the movement of the slug will occur mainly by bulk transport driven by the turbulent elements, with relatively little dispersion or decrease in concentration within the slug. If the slug is instead embedded in eddies of approximately the same size, diffusion will be quite rapid and the concentration within the slug will decrease rapidly.]

[The downstream distribution of the spilled substance after it has been dispersed is frequently expressed in terms of exposure, or the time integral of the concentration as the slug passes the observation point.]

It is of interest to note the application of instantaneous release phenomena in the field of nuclear engineering. [Although the so-called "hot-cloud" accident, an instantaneous release of all the nuclear and chemical energy of a reactor to the atmosphere, is no longer considered credible because of reactor-containment features, other possibilities for generating sources of this kind exist. Some examples are the short-term controlled release of fission products from a contained accident, explosive accidents occurring during nuclear-fuel reprocessing, accidental criticalities, launching-pad accidents involving nuclear (or chemical) rockets, and non-nuclear explosions of all kinds.]

b. The Continuous Point Source

[Text of the following three paragraphs appearing in brackets was abstracted from a discussion given in reference[17] pertaining to dispersion in air; although the context has been modified for the purpose of this report, much of the concept and text have remained unchanged.]

[Continuous point sources give good approximations to tank venting from small holes, fissures or pipes. The approximation given by the point source for the true source configuration becomes increasingly better as the distance, at which the concentration is observed, becomes large compared with the dimensions of the source.]

[A continuous release may be considered to be made up of an infinite number of slugs released sequentially with a vanishingly small time interval between slugs. Initially each slug moves with the river current at the moment of release. The quantity of material released is usually expressed in terms of a release rate and the downstream material distribution is usually expressed in terms of average concentration over the period of release. Linear dimensions of the dispersing material perpendicular to the longitudinal axis, running downstream from the spill site, are often given in terms of the standard deviation of the concentration distribution since the average cross-sectional distribution, in the absence of significant boundary effects, is usually close to a normal curve with boundaries at infinity.]

[Since the plume from a continuously maintained point source expands both laterally and vertically with downstream distance from the source, the center-line concentration along the downstream axis from the spill point will drecrease continuously with distance. The rate at which this decrease occurs will depend on the magnitude of the turbulence.]

Further detailed discussion is given in this reference[17] with respect to time-averaging and the variations in wind velocity and direction which are particularly significant for airborne phenomena. For the purpose of the water dispersion model, an adequate concept of a continuous release is that of a series of an infinite number of instantaneous releases, creating a plume in the downstream direction of a dispersing chemical mass. Concentrations are reduced with distance from the spill in both the longitudinal and cross-stream directions; however, for long duration events, the concentration obtained at any observation point is a steady state value, and not a function of time.

c. Distributed Sources

[Text of the first three paragraphs following and appearing in brackets was abstracted from a discussion given in reference[17] pertaining to dispersion in air; the text has remained substantially unchanged.]

[Although instantaneous and continuous point sources have been extensively utilized in modeling or describing a broad range of diffusion phenomena, a number of other source configurations have received attention also. The instantaneous line source is a fairly common type that can be approximated by a continuously emitting, rapidly moving system, such as a crop-spraying aircraft. Such a line is usually thought of as extending to infinity in both directions so that along-line diffusion may be neglected, and the decrease of concentration with travel distance is entirely explained by diffusion in the vertical and along-wind directions.]

[Another source type, the continuous line source, may be approximated by a busy highway or a line of closely spaced vents. Since the release is continuous, the sampling time is germane.] Line sources are often assumed in modeling water dispersion from sewage outfalls.

[The continuous area source, although as yet of minor importance in nuclear problems, is receiving increasing attention in the urban air-pollution field. A city, with its multitude of pollutant-emitting sources, is the most common and characteristic representative of the area source.]

(1) Principle of Superposition

The distributed sources, which may also be instantaneous or continuous, are distinguished from the point sources by a spatial dimension or distribution at the release location. Depending on the nature of the release this variation may be assumed to take place in one, two, or three dimensions. In some situations, such as the discharge of sewage from a fixed system of discharge pipes, the geometry of the discharge distribution may be obtained or known with some degree of accuracy. In other cases, however, such as associated with the accidental and possibly violent release of a chemical in large quantities, there will be considerable uncertainty in determining the initial geometry of release. Also, it should be noted that at large distances from the location of a spill, the effects of the initial distribution will become diminished, and the resulting concentrations will approach those produced from a point source. However, it is the benefit of obtaining model representations in which the concentrations at the spill location remain finite and are susceptible to arbitrary initialization that prompts continued interest for simplified cases.

As the discussion in the preceding section implied, the bahavior of a continuous point source release can be modeled by integrating the contributions of a series of instantaneous point sources over time, applying the principle of superposition since the diffusion equation is linear. Thus, any arbitrary continuous release rate behavior may be assumed (whether or not justified by observational data), although the nature of the integration may not lead to closed form solutions.

In an analogous manner, the contributions from a series of instantaneous sources with origins at different locations may be integrated with respect to the spatial dimensions to develop expressions for concentrations from instantaneous distributed sources of any arbitrary configuration. Finally, these expressions may then be integrated with respect to time-varying release conditions to obtain concentration functions for continuous distributed sources.

(2) Virtual Sources

Since in many cases of practical interest the integrations required to obtain superimposed solutions are not readily carried out, distributed sources can frequently be approximated by assuming a point source to be located at some distance removed upstream from the location of the distributed source. The offset distance may either be arbitrarily specified, or determined such that at the time the slug from the virtual source reaches the actual spill location, some characteristic of the dispersing chemical from the virtual source can be related to a characteristic of the distributed source. Elapsed time from the start of the distributed spill is then given as the elapsed time from the start of the virtual spill, less the travel time from the location of the virtual spill to the location of the actual spill.

(3) Modified Solution

Since there may be considerable uncertainties in determining the configuration of a distributed spill and evaluating the resulting integrals may be quite complex, an alternate approximation may be taken. This method, illustrated by example in Section II, paragraph 3.d, essentially entails adding an artificial term to the denominator of the concentration equations for an instantaneous point source, such that the initial concentration at the spill location may be set to any arbitrarily desired value. The initial condition still retains the nature of a point source, that is, initial concentrations at locations away from the origin are zero, so that an initial spatial distribution is not obtained. Also, as a result, conservation of mass is not maintained by this method of solution; that is, integration of concentration with respect to spatial coordinates will not yield the total mass of chemical spilled instantaneously until some time after the occurrence of the spill. This could, however, be considered as an alternative to the representation of an instantaneous spill.

d. Chemical Degradation on Release

The form of the continuity or governing diffusion equation provides for limited modeling of non-conservative effects such as decay or degradation. The rate of loss is assumed to be proportional to the concentration of the substance, and the factor of proportionality is taken as a decay or rate constant, k, having dimensions of $(\text{time})^{-1}$.

Solutions of the diffusion equation for the Gaussian model give the result, for an instantaneous release, that the concentration distributions depend on the total mass of substance in the diffusing media, given in the form:

$$M(t) = M(0)\, e^{-kt} \tag{6}$$

where

$M(0)$ = total mass of chemical, released instantaneously into the environment at time $t = 0$

$M(t)$ = total mass of substance remaining in the environment after an elapsed time t from the release

k = decay factor or rate constant for overall degradation of chemical in environment

t = elapsed time from release.

This results in a description of the time-dependent degradation process that is simply related to the elapsed time from release and is a usual limitation of a Gaussian model. The influences of chemically interacting sources or source components of formation reactions involving several primary or secondary pollutants, or the photochemical effects are normally beyond the scope of these models[18].

The ratio of the total amount of substance in the diffusing media at any time to the amount initially present can be written in non-dimensional form, letting the ratio be denoted by α, as:

$$\alpha(t) = \frac{M(t)}{M(0)} = e^{-kt} \tag{7}$$

where values of the exponential function $\alpha(t)$ vary from $\alpha(0) = 1$ to 0 as t becomes very large; values of $\alpha(t)$ are plotted in Figure 4 for values of kt from 0.0 to 3.0.

If no decay or degradation is assumed to take place, then for $k = 0$, the value of $\alpha(t)$ is 1.0 for all values of time; therefore, the total amount of substance in the environment is constant and equal to the amount originally released at time $t = 0$.

For non-zero values of k, decay occurs rapidly over a short range of values of kt. It is interesting to observe that the concentration distributions are proportional to the total mass in the environment. The ratio varies from 1.0 for $kt = 0$ to approximately 0.05 for $kt = 3.0$ (only 5 percent of the mass originally released remains at $kt = 3$). Thus, for large values of k, the time over which finite concentrations may exist will be limited.

Half the mass originally released remains at a time $t_{1/2}$ given by:

$$\alpha(t_{1/2}) = \frac{1}{2} = e^{-kt_{1/2}} \tag{8}$$

so that

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \tag{9}$$

where $t_{1/2}$, the time for one-half of the original amount of substance to decay, is known as the half-life. If half-life data is available, the appropriate rate constant for use in the spill model is given by:

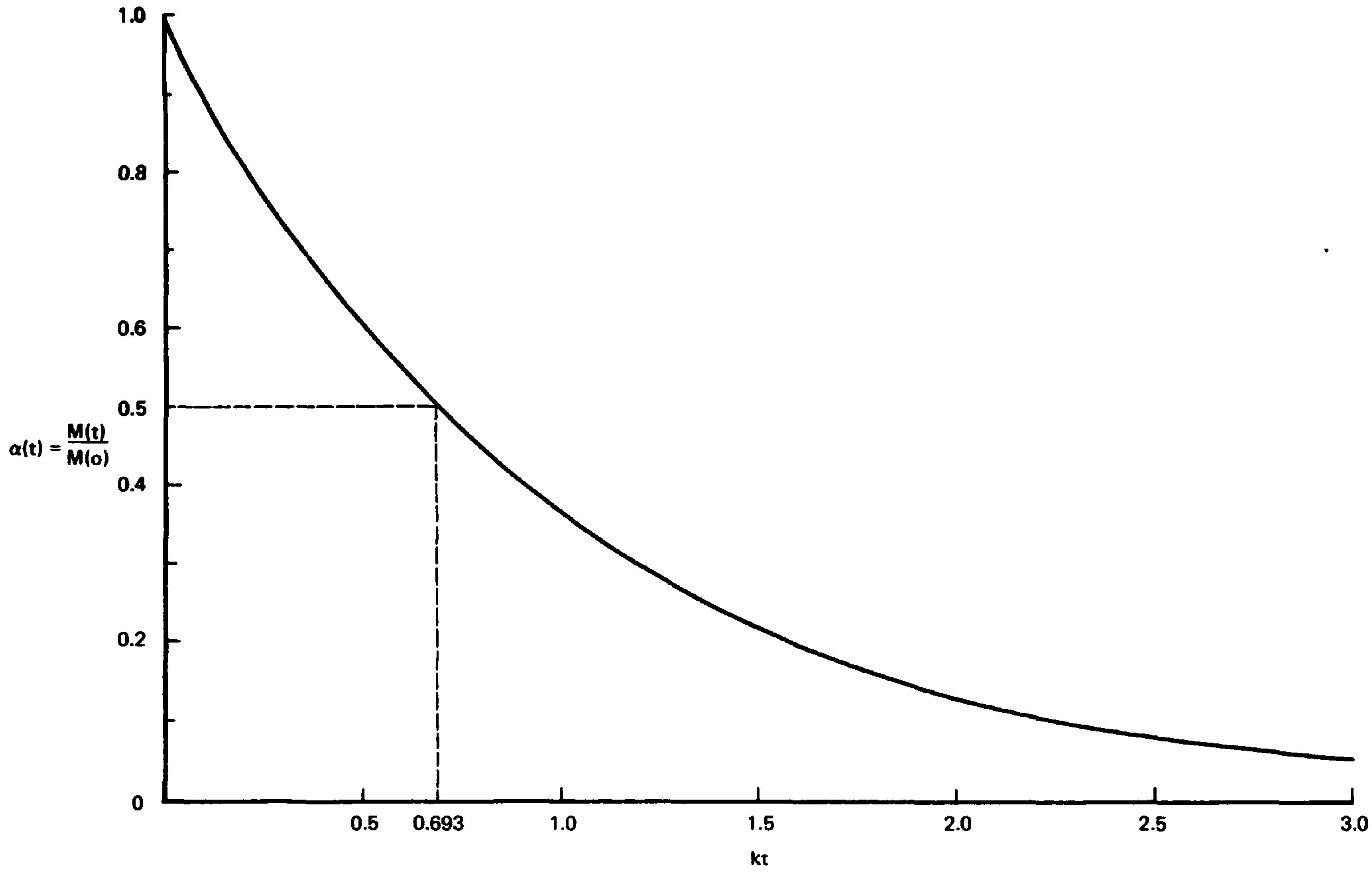


Figure 4. Decay Function $\alpha(t) = e^{-kt}$

$$k = \frac{0.693}{t_{1/2}} \tag{10}$$

where the units of the decay constant are the reciprocal of the units in which the half-life is given assuming that the data approximates a first order decay.

Reduction of substance in the environment may be the result of more than one decay process. If separate degradation processes (such as oxidation, biodegration, hydrolysis, and photolysis) are estimated in terms of separate rate constants, the overall decay coefficient k is obtained as the sum of the individual rate constants. The half-life of the material is obtained as ln(2) divided by the sum of the rate constants. If the degradation processes are described by separate half-lives, then conversion to individual rate constants is required before the summation.

As discussed in greater detail in Section I, paragraph 2, half-life estimates for the degradation of hydrazine fuels in the aquatic environment appear to be on the order of 10 to 1000 hours. Taking a half-life of 100 hours gives a nominal value for the decay coefficient of 6.93×10^{-3} hours or 1.15×10^{-4} minutes. At this value, an elapsed time of approximately 430 hours would be required to reduce the total amount of a spilled substance to 5 percent of its initial mass.

However, experimental studies[19] have concluded that slow degradation rates occur in the absence of added catalysts, and, as a result, that hydrazine should be assumed to be conservative in modeling aqueous spills. Furthermore, to the extent that decomposition in water does occur, many of the reaction products may also be harmful; since the model does not have the capability of including reaction products, further justification is suggested for the conservative approach to ignore the separate reaction products and use a decay coefficient of zero.

e. Conservation of Mass

(1) Instantaneous Releases

Where the actual elapsed time of release, from the time the spill starts to the time the discharge ceases, is short with respect to the movement of the spilled chemical in water, the discharge of the chemical can be assumed to occur instantaneously. This is modeled as a release of a fixed mass of substance, M, which occurs at time t = 0 (t is elapsed time from start of spill).

In the absence of chemical degradation processes, the total quantity (mass) of a substance introduced into the environment as an instantaneous release is defined as:

$$\begin{aligned} M(t) &= 0, \qquad t < 0 \\ M(t) &= M(0), \qquad t \geq 0 \end{aligned} \tag{11}$$

where M(t) denotes the total quantity of mass in the environment. Since the resulting concentration distributions are directly proportional to the quantity of mass, for Gaussian distributions, it can be seen that this gives concentration values of zero for values of elapsed time t less than zero, as would be expected.

Modeling the effects of degradation or decay processes in the aquatic environment assumes that the overall degradation occurs exponentially, giving for the instantaneous release:

$$M(t) = 0, \qquad t < 0$$

$$M(t) = M(0)\, e^{-kt}, \qquad t \geq 0 \tag{12}$$

where k is the overall decay rate constant and has units of $(\text{time})^{-1}$.

Since $e^{-kt} = 1$ for either $k = 0$ or $t = 0$, only the latter expression in Equation (12) for the total mass is necessary, since it correctly reduces to the conservative case with $k = 0$.

At any time t conservation of mass will hold if the integral of the concentration distribution, in time and space, over the spatial dimensions of the diffusing water body, is equal to the total mass of dispersing substance in that water body, given as a function of time in the form above.

The expression for the total mass M(t) in the aquatic environment can also be written in terms of the half-life of the chemical using:

$$k = \frac{\ln 2}{t_{1/2}} \qquad \text{and} \qquad \beta = \frac{t}{t_{1/2}} \tag{13}$$

to obtain

$$M(t) = \frac{M}{2^{\beta}} = M \cdot 2^{-\beta} \tag{14}$$

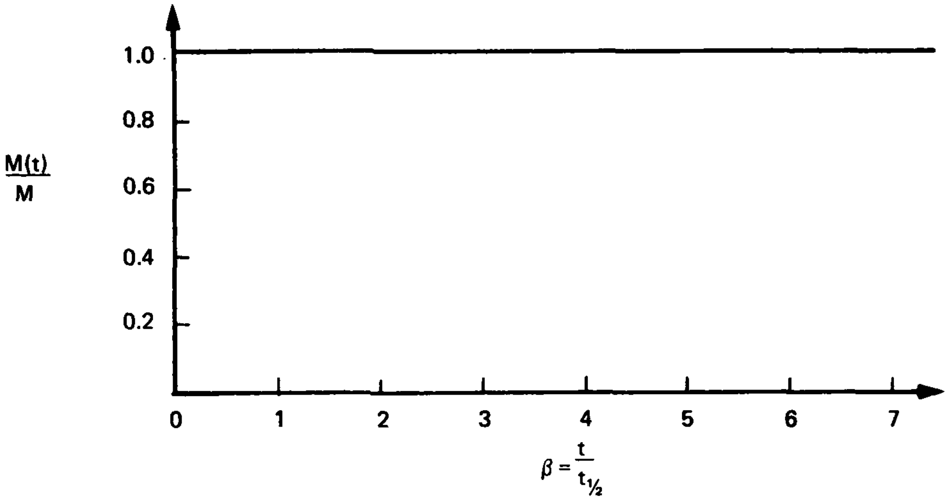
where the term β is used here to denote the ratio of elapsed time to the chemical half-life and M(0) is written simply as M. This provides a useful means for estimating the time scale of interest for a dispersing chemical initially released instantaneously. A few values of the term $2^{-\beta}$ tabulated below:

β	$2^{-\beta}$
0	1.0
1	0.5
2	0.25
3	0.125
4	0.0625
5	0.03125
6	0.015625
7	0.0078125

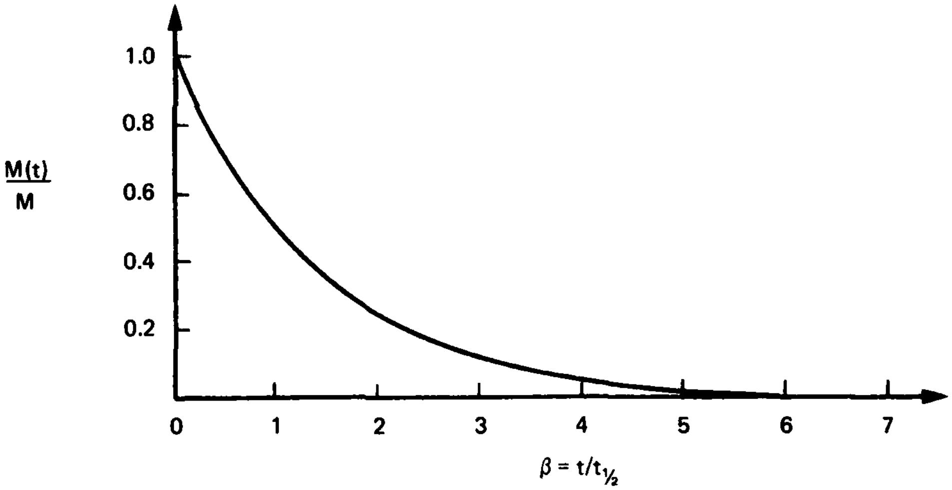
show that after each interval of elapsed time equal to the half-life of the chemical, the total amount of dispersing mass in the environment is reduced by 50 percent, and that the mass remaining after seven multiples of the half-life is less than 1 percent of the mass orginally released. Figure 5 illustrates the time history for the total mass of chemical in the aquatic environment for different instantaneous release conditions.

(2) Continuous Releases

When the actual elapsed time of release is large with respect to the decay or movement of the spilled chemical in water, the discharge of the chemical is modeled using the rate of release of the substance instead of the total



(a) Instantaneous release, no decay (k = 0)



(b) Instantaneous release with decay (k > 0)

Figure 5. **Total Dispersing Mass for Instantaneous Releases**

quantity released, M. Since the method of solution employs superposition of the effects of a series of instantaneous releases, consideration of any functional form for the time history of the continuous release is feasible, at least theoretically. However, the resultant numerical integration to describe an arbitrary time-varying release would significantly increase the complexity of the model, and substantial uncertainty exists in the degree of accuracy with which these variations can be determined for the types of releases considered for this model.

A simplifying assumption is introduced that a continuous spill is assumed to occur at a constant rate. The spill or discharge is assumed to start at elapsed time $t = 0$, and continue until a later time t_{mt}. The discharge rate is taken as a constant, $\dot{M}$ (mass/time), during this interval, and zero otherwise. Transient effects at the start and cessation of the spill are not modeled.

Given these assumptions, the total amount of substance discharged by a continuous release to the environment, $Q(t)$ (units of mass), is modeled as a function of elapsed time by:

$$\begin{aligned} Q(t) &= 0, && t < 0 \\ Q(t) &= \dot{M}\, t, && 0 \le t \le t_{mt} \\ Q(t) &= 0, && t > t_{mt} \end{aligned} \tag{15}$$

If the total quantity released during the spill, $Q(t_{mt})$, is denoted by M for consistency with the total mass released from an instantaneous source, then the duration or release time for a continuous source is obtained from:

$$t_{mt} = \frac{M}{\dot{M}} \tag{16}$$

(a) Conservative Substance

In the absence of assumed decay or chemical degradation processes, the entire amount of substance introduced continuously will remain in the environment. For use in the mass balance, this gives the time history for the total mass of chemical substance in the aquatic environment as:

$$M(t) = 0, \qquad t < 0$$

$$M(t) = \dot{M}\, t, \qquad 0 \leq t \leq t_{mt}$$

$$M(t) = \dot{M}\, t_{mt}, \qquad t > t_{mt} \tag{17}$$

so that the total dispersing mass increases linearly with elapsed time, until t reaches a value of t_{mt} after which time M(t) has a constant value of $\dot{M}\, t_{mt}$. If the total mass spilled either instantaneously or continuously is the same, then in the absence of decay, for times greater than t_{mt}, the total dispersing mass in the environment from a continuous spill is the same as that from an instantaneous spill.

(b) Decay Processes

The expression for the total amount of substance remaining in the environment, resulting from a continuous release when decay or degradation occurs in the environment, is obtained by treating the continuous release as a series of instantaneous releases. Two cases are of interest: one for observation times during the release interval and the other after the spill has ceased. (Observation times prior to the start of the spill correspond to zero mass.)

At time t, the total mass of chemical in the water will depend on the total quantity that has been released from the start of the spill at t = 0 up to the current time t. Considering any elapsed time τ within this range, the incremental amount of material released during a small interval of time $d\tau$ is given by $\dot{M}\, d\tau$.

Considered as an instantaneous release, this incremental mass will decay in the environment over time, contributing to the total mass at time t an incremental amount given by $\dot{M}\, d\tau\, e^{-k(t-\tau)}$. Limits are implied in that the contribution is zero if $\tau > t$, $\tau > t_{mt}$ and $\tau < 0$.

For values of time less than t_{mt}, the total quantity of substance in the environment is obtained as the sum of the contributions from each of the infinitesimal instantaneous releases occurring over the interval 0 to t, or the integral:

$$M(t) = \int_0^t \dot{M}\, e^{-k(t-\tau)}\, d\tau, \qquad 0 \leq \tau \leq t, \qquad t \leq t_{mt} \tag{18}$$

This integral is evaluated to give:

$$M(t) = \frac{\dot{M}}{k}\left[1 - e^{-kt}\right], \qquad t \leq t_{mt} \tag{19}$$

When the elapsed time of interest, t, is greater than the time for the continuous release to take place, t_{mt}, the contributions of the infinitesimal instantaneous releases at values of $\tau > t_{mt}$ are zero, and the integral simply becomes:

$$M(t) = \int_0^{t_{mt}} \dot{M}\, e^{-k(t-\tau)}\, d\tau, \qquad t > t_{mt} \tag{20}$$

This is evaluated to yield:

$$M(t) = \frac{\dot{M}}{k}\left[e^{-k(t-t_{mt})} - e^{-kt}\right], \quad t > t_{mt} \tag{21}$$

Due to the appearance of the decay coefficient in the demoninator, neither of these expressions for the total mass directly simplifies to the previous equations obtained for conservative substances, Equation (17) ; however, series expansion of the exponential terms can be used to demonstrate the consistency of these expressions in the limit as $k \to 0$.

(c) Long Duration Continuous Spills

If the value of t_{mt} is very large so that the continuous spill occurs at a constant rate for a long time, the total mass of the substance in the environment given by

$$M(t) = \frac{\dot{M}}{k}\left[1 - e^{-kt}\right] \tag{22}$$

approaches a steady state value, for large observation times, of:

$$\lim_{t\to\infty} M(t) = \frac{\dot{M}}{k} \tag{23}$$

For small values of time the equation gives M(0) = 0 so the total mass of the dispersing chemical increases gradually from 0 to the limit value of $\dot{M}/k$. This mass time history is illustrated by writing:

$$M(t) = \frac{\dot{M}}{k} - \frac{\dot{M}}{k}e^{-kt} \tag{24}$$

and, observing the behavior of the decaying exponential term from Figure 4, it can be seen that the total mass in the environment reaches 95 percent of its steady state value at $kt \sim 3.0$.

Since the decay coefficient can be written in terms of the half-life, at kt = 3.0, then

$$3.0 = kt = \frac{t}{t_{1/2}} \ln 2 \tag{25}$$

so that $t = 4.3\ t_{1/2}$. This indicates that if the duration of a continuous release is greater than four times the half-life of the discharged substance in the aquatic environment, then the total amount of dispersing mass in the environment has approximately reached the steady state value, which is also the maximum attainable value, at the given release rate of $\frac{\dot{M}}{k}$, or equivalently, $\dot{M}\ t_{1/2}/\ln 2$ at the given release rate.

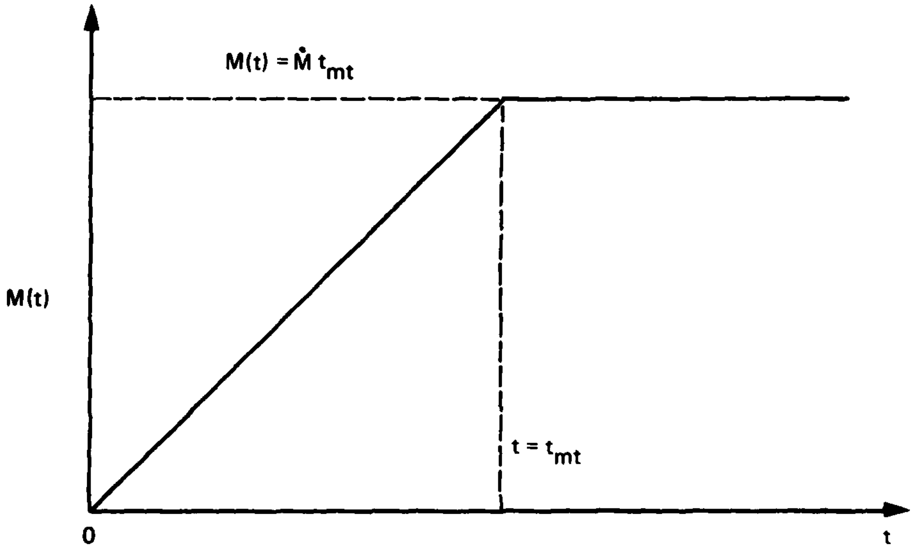
Writing the expression for the total mass M(t) dispersing in the aquatic environment in terms of the half-life and the ratio β of elapsed time to half-life gives:

$$M(t) = \dot{M}\ t_{1/2} \cdot \frac{1}{\ln 2} \cdot \left[1 - 2^{-\beta}\right] \tag{26}$$

so that the value of M(t) can be expressed in terms of $\dot{M}$, $t_{1/2}$, and β. Selected values are tabulated below and illustrated in Figure 6.

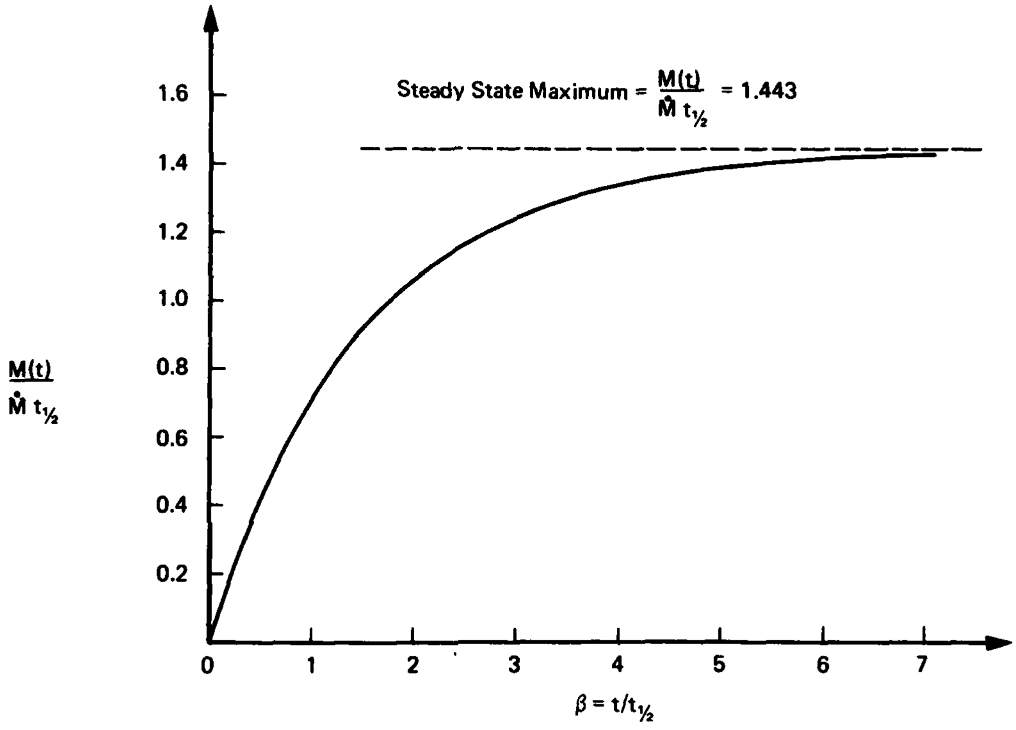
$\beta = \frac{t}{t_{1/2}}$	$M(t)/\dot{M}\ t_{1/2}$
0	0.0
1	0.721
2	1.082
3	1.262
4	1.353
5	1.398
6	1.420
7	1.431

For very large values of β, the steady state value of M(t) is obtained as $1.443\ \dot{M}\ t_{1/2}$. Therefore, for long duration releases, the maximum quantity of mass dispersing in the environment is constant and depends only on the release rate and half-life but is independent of the duration of the release.



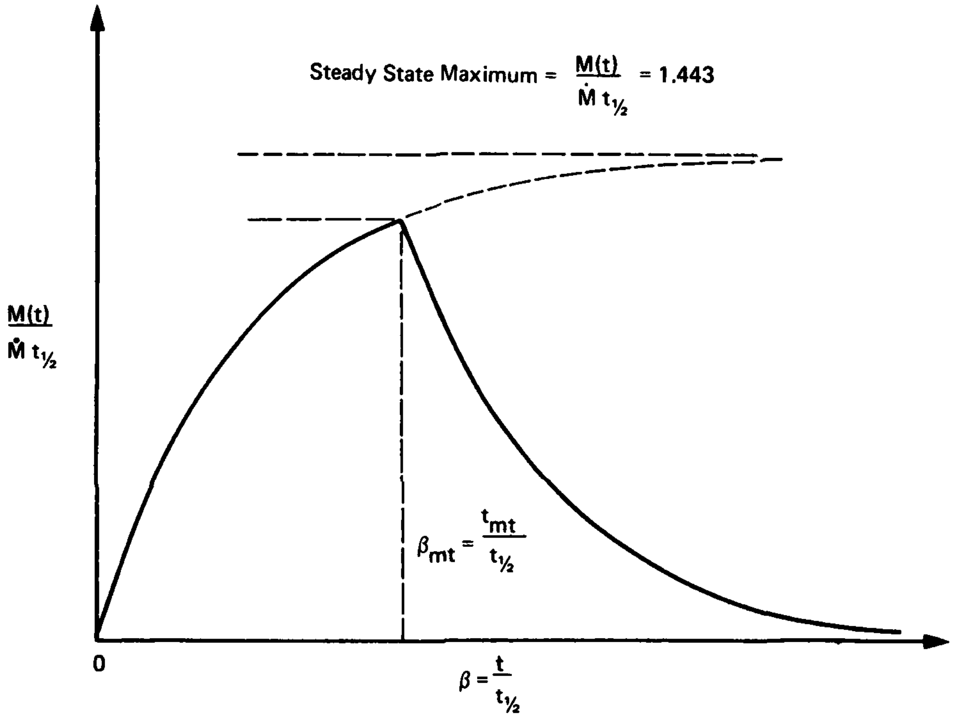
(a) Continuous release, no decay (k = 0)

Figure 6. Total Dispersing Mass for Continuous Releases



(b) Continuous release of long duration with decay ($k > 0$)

Figure 6. Total Dispersing Mass for Continuous Releases (Continued)



(c) Continuous release of short duration with decay ($k > 0$)

Figure 6. Total Dispersing Mass for Continuous Releases (Concluded)

(d) Short Duration Continuous Spills

If the observation time t is large with respect to the time at which the continuous spill stops, t_{mt}, then writing the expression for the total mass of the discharged substance in the environment as:

$$M(t) = \frac{\dot{M}}{k}\left[1 - e^{-kt_{mt}}\right] \cdot e^{-k(t-t_{mt})}, \qquad t > t_{mt} \tag{27}$$

shows that the behavior for $t > t_{mt}$ is that of a fixed amount of mass $\frac{\dot{M}}{k}\left[1 - e^{-kt_{mt}}\right]$ remaining in the environment at the end of the continuous discharge, all decaying exponentially from the moment the spill stops according to $e^{-k(t-t_{mt})}$. This decay behavior is analogous to that for an instantaneous release, except that the total quantity of mass from a continuous release that is decaying for $t > t_{mt}$ has dispersed to some extent, and the time history of the release results in a larger residual mass than that remaining at the same time from an instantaneous discharge:

$$M(t_{mt}) = M \cdot e^{-kt_{mt}} \quad \text{(Instantaneous)} \tag{28}$$

$$M(t_{mt}) = \dot{M}\, t_{mt} \cdot \left[\frac{1 - e^{-kt_{mt}}}{kt_{mt}}\right] \quad \text{(Continuous)} \tag{29}$$

Considering the residual mass as a function of the total mass discharged, so that $\dot{M}\, t_{mt}$ is equivalent to M, it can be shown that the two expressions are only approximately equivalent for values of kt_{mt} less than 0.5.

As the duration of the spill, t_{mt}, becomes small the continuous release expression for the quantity of dispersing mass, M(t), correctly approaches zero.

Writing the expression for the total dispersing mass M(t) as a function of half-life and the ratio β of elapsed time to half-life gives, for time after the release has stopped:

$$M(t) = \frac{\dot{M}\, t_{1/2}}{\ln 2} \left[1 - 2^{-\beta_{mt}} \right] \cdot \frac{1}{2^{(\beta - \beta_{mt})}} \tag{30}$$

where $\beta_{mt} = \dfrac{t_{mt}}{t_{1/2}}$ and $\beta \geq \beta_{mt}$. Since the first part of this expression simply gives the total dispersing mass at $t = t_{mt}$, this can be denoted as $M(t_{mt})$ to yield:

$$M(t) = \frac{M(t_{mt})}{2^{(\beta - \beta_{mt})}}, \qquad \beta \geq \beta_{mt} \tag{31}$$

which can easily be seen to be in the same form as the similar expression [Equation (14)] for an instantaneous release. This behavior is illustrated in Figure 6(c). Note that the abscissas of Figure 6(a) and (c) are not scaled since the relationship between t_{mt} and $t_{1/2}$ is arbitrary.

As for instantaneous releases, at any time t conservation of mass will hold if the integral of the concentration distribution, in time and space, over the spatial dimensions of the diffusing water body, is equal to the total mass of dispersing substance in that water body, given as a function of time in one of the forms above.

(e) Instantaneous Behavior of Continuous Release

In the preceding subsection, the analogous expressions for the total quantity of dispersing mass suggests that for observation times sufficiently greater than the duration of a continuous release, the release can be considered as an equivalent instantaneous release of source strength $\dot{M}\, t_{mt}$. Use of the instantaneous equations, in the region of these observation times, would enable the model to depict the concentration time history at the observation point as the equivalent slug passes rather than just the steady state value for the continuous case (since rise time effects are ignored).

The criteria that has been suggested and used previously[12] is that if the elapsed time is greater than five times the spill duration an equivalent instantaneous release is assumed. However, it has also been suggested that other criteria may be more appropriate and it has been shown above that the total quantities of dispersing mass are roughly equivalent only for a small range of values of kt_{mt}. For the case of a flowing river, the instantaneous description may be more appropriate than the continuous description when the advection length of the spill (t_{mt}/u) is comparable to, or smaller than, the diffusion width of the spill $(\sqrt{e_y t}$ or $\sqrt{e_z t})$[20]. Thus, the selection criteria may require further refinement to more adequately include the effect of the values of x, u, e_y and e_z, in addition to t and t_{mt} (where e_y and e_z are turbulent dispersion coefficients).

Further, the method utilized contemplates changing the nature of the assumed release condition as elapsed time varies for any spatial coordinates of the observation point. It appears from this that discontinuities may be introduced as a result of the transition between the continuous and instantaneous descriptions.

f. Summary of Discharge Equation

Summarized in Table 3 from preceding subsections are the expressions defining the total quantity of dispersing chemical mass in the environment as a function of time from a release occurring at $t = 0$.

These expressions for the total quantity of dispersing mass as a function of time are illustrated in Figures 5 and 6. The important characteristics resulting from the assumed release conditions are summarized below:

(1) Instantaneous Release, No Decay

- The total mass discharged to the environment is M.
- The maximum value of the total mass dispersing in the environment is M, reached at $t=0$ and constant thereafter.

(2) Instantaneous Release, with Decay

- The total mass discharged to the environment is M.
- The substance decays in the environment according to a rate constant of:

$$k, \text{ or } k = \frac{\ln 2}{t_{1/2}} \tag{32}$$

or, according to a half-life of:

$$t_{1/2}, \text{ or } t_{1/2} = \frac{\ln 2}{k} \tag{33}$$

where $t_{1/2}$ is in units consistent with k and $\ln 2 = 0.69315$.

TABLE 3. SUMMARY OF DISCHARGE EQUATIONS

		Total Dispersing Mass M(t)		
Type of Release	Elapsed Time	No Decay (k=0)	With Decay (k>0)	
Instantaneous	$t < 0$	0	0	0
	$t \geq 0$	M	$M e^{-kt}$	$= \frac{M}{2^{\beta}}$
Continuous	$t < 0$	0	0	0
	$0 \leq t \leq t_{mt}$	$\dot{M}\, t$	$\frac{\dot{M}}{k}\left[1 - e^{-kt}\right]$	$= \dot{M}\, t_{1/2} \cdot \frac{(1 - 2^{-\beta})}{\ln 2}$
	$t > t_{mt}$	$\dot{M}\, t_{mt}$	$\frac{\dot{M}}{k}\left[1 - e^{-kt_{mt}}\right] \cdot e^{-k(t-t_{mt})}$	$= \dot{M}\, t_{1/2} \cdot \left(\frac{1-2^{-\beta_{mt}}}{\ln 2}\right) \cdot \frac{1}{2^{(\beta-\beta_{mt})}}$
	$t > t_{mt}$	$\dot{M}\, t_{mt}$	$M(t_{mt}) \cdot e^{-k(t-t_{mt})}$	$= \frac{M(t_{mt})}{2^{(\beta-\beta_{mt})}}$

Using $k = \frac{\ln 2}{t_{1/2}}$, $\beta \frac{t}{t_{1/2}}$ and $\beta_{mt} = \frac{t_{mt}}{t_{1/2}}$

- The maximum value of the total mass dispersing in the environment is M, reached at t=0.
- The time required for the dispersing mass to be reduced to 1 percent of its maximum value in the environment is:

$$t = \frac{2 \ln 10}{k} = \frac{2 \ln 10}{\ln 2} \cdot t_{1/2} \tag{34}$$

  and the total mass remaining in the environment at that time is 0.01 M, where ln 10 = 2.30259.

(3) Continuous Release, No Decay

- The total mass discharged to the environment is $\dot{M}\ t_{mt}$, or M.
- This quantity is released at a rate $\dot{M}$ for a duration of t_{mt}.
- The maximum value of the total mass dispersing in the environment is M, reached at time = t_{mt} and constant thereafter.

(4) Continuous Release, With Decay

- The total mass discharged to the environment is $\dot{M}\ t_{mt}$, or M.
- This quantity is released at a rate $\dot{M}$ for a duration of t_{mt}.
- The substance decays in the environment according to a rate constant of:

$$k, \text{ or } k = \frac{\ln 2}{t_{1/2}} \tag{35}$$

  or according to a half-life of:

$$t_{1/2}, \text{ or } t_{1/2} = \frac{\ln 2}{k} . \tag{36}$$

- For releases of very long durations at this rate of release and substance half-life, the largest possible quantity of total mass dispersing in the environment is:

$$M(t) = \dot{M}\ t_{1/2} \frac{1}{\ln 2} = 1.443\ \dot{M}\ t_{1/2} \tag{37}$$

  under steady state conditions as shown in Figure 6b.

- For continuous release conditions of fixed duration, the maximum amount of total mass dispersing in the environment is:

$$M(t_{mt}) = \frac{\dot{M}}{k}\left(1 - e^{-kt_{mt}}\right) \tag{38}$$

and this occurs at time t_{mt} as shown in Figure 6c.

- The total time required for the dispersing mass to be reduced to 1 percent of its maximum value in the environment is:

$$t = \frac{2 \ln 10}{k} + t_{mt} \tag{39}$$

and the total mass remaining in the environment at that time is $0.01\ M(t_{mt})$.

SECTION II

THE DIFFUSION EQUATION AND ELEMENTARY SOLUTIONS

1. THREE-DIMENSIONAL DIFFUSION EQUATION

The general three-dimensional diffusion equation describing the movement of a chemical mass in a receiving water body is given as:

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z}$$

$$= \frac{\partial}{\partial x}\left(e_x\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(e_y\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(e_z\frac{\partial c}{\partial z}\right) - kc \qquad (40)$$

The spatial coordinates x, y, z are taken to form the usual right-handed system, and the components of the bulk fluid velocity along these axes are u, v, w, respectively. The concentration, c, determined by this equation is obtained as a function of spatial coordinates and time, i.e., $c = c(x,y,z,t)$, given in units of mass per unit volume.

The governing diffusion or continuity equation is based on a material balance and determines the resulting movement and depletion of a chemical mass introduced into a receiving water body.

The rate of change of the mass per unit volume with time, $\frac{\partial c}{\partial t}$, is governed by the migration of the mass within the fluid volume and the production or depletion of the chemical mass by reaction occurring within the fluid. The reaction term in the above equation is given as -kc so that only first order processes proportional to the concentration are included. The constant of proportionality is given by a rate constant, k, and the sign of the term is negative for net depletion of the mass by chemical decay or degradation in the aquatic environment.

The remaining terms in the diffusion equation reflect the migration of the mass within the fluid volume according to three fundamentally different types of transport.

Convection or advection describes the movement of the chemical in the water produced as a result of the bulk flow or movement of the receiving water body and is governed by the terms:

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} + w \frac{\partial c}{\partial z} \tag{41}$$

where the velocities u, v, w describe the bulk flow of the receiving water body in three dimensions and are, in the general sense, time-dependent to describe both the spatial and temporal motion of the fluid. For river bodies of practical interest, the predominating effect of bulk flow occurs in the longitudinal direction (x), and the cross-current velocity components in v and w are neglected.

The remaining terms of the diffusion equation:

$$\frac{\partial}{\partial x}\left(e_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(e_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(e_z \frac{\partial c}{\partial z}\right) \tag{42}$$

are used to describe the migration of the chemical mass in the fluid volume according to two entirely different means, yet governed by the same form of the equation: molecular diffusion and turbulent dispersion. In the case of laminar fluid flow the diffusion terms account for the migration of the mass as a result of concentration gradients (molecular diffusion). If turbulence is present, the diffusion terms account for the migration of the mass as a result of the turbulent motion of the receiving water body. The coefficients used to describe each type of migration are vastly different, as are the resulting movements. In general, molecular motion takes place on a microscopic scale, compared to the macroscopic scale of turbulent motion. The spread of any pollutant in a body of water in the environment takes place in a flow field that is almost certainly turbulent, and the effects of molecular diffusion are usually negligible with respect to turbulent motion.

The presence of a concentration gradient in the receiving water body results in a migration or diffusion of the chemical mass that tends to eliminate the gradient. This migration, which results from the molecular motion and occurs independently of pressure or temperature gradients, gravitational or other body forces, or bulk fluid motion, is observed as molecular diffusion. In general, the molecular diffusion coefficient, written as D, is often taken as a constant and non-isotropic variations assumed to be negligible so that the diffusion equation is written using

$$e_x = e_y = e_z = D \tag{43}$$

Mass transfer in turbulent fluid motion is essentially a mixing process and is represented in the diffusion equation by the turbulent dispersion coefficients e_x, e_y, and e_z. Under non-isotropic conditions, turbulence-induced migration will occur at different rates in different coordinate directions, and the values of the coefficients in each principal direction may differ by several orders of magnitude. The magnitude of the turbulent dispersion coefficients are usually many times larger than molecular diffusivity.

a. Turbulent Dispersion Coefficients

Estimation of turbulent dispersion coefficients in natural water bodies is a topic which has generated an extensive literature with proposed formulas based on fundamental theories of mixing by random motions, dimensional analysis and/or similarity theory, and empiricism. For practical dispersion modeling, the most successful formulas are based on a mixture of similarity theory and empirical studies. An example of this approach is the mixing length hypothesis used to estimate dispersion coefficients, e, in boundary layers. Similarity theory indicates that:

$$e \propto U_* l \tag{44}$$

where U_*, known as the shear velocity, is generally assumed to be proportional to the velocity far from the boundary (U_∞) and l is the mixing length, which is proportional to the distance to the boundary (d_b). Empirical studies, which may be laboratory- or field-based, establish the proportionality coefficients relating e to observable properties of the flow field, U_∞ and d_b. The methods used to compute the turbulent dispersion coefficients in three dimensions (e_x, e_y, e_z) are described in the separate sections of this report pertaining to each model.

b. Transformation of Diffusion Equation

The generalized three-dimensional form of the diffusion equation governs the behavior of the concentration as a function of spatial coordinates and time: c(x,y,z,t). If the concentration is written as the product of two functions:

$$c(x,y,z,t) = q(x,y,z,t)\ e^{-kt} \tag{45}$$

substitution in a diffusion equation for c, which contains a reaction term, will lead to a similar diffusion equation for q in which the reaction term disappears.

This follows since

$$\frac{\partial c}{\partial x} = \frac{\partial q}{\partial x}\ e^{-kt} \tag{46}$$

$$\frac{\partial}{\partial x}\left(e_x \frac{\partial c}{\partial x}\right) = \frac{\partial}{\partial x}\left(e_x \frac{\partial q}{\partial x}\right) e^{-kt} \tag{47}$$

and so forth for the coordinates y and z, and

$$\frac{\partial c}{\partial t} = \frac{\partial q}{\partial t}\ e^{-kt} - k\ q\ e^{-kt} = e^{-kt}\ \left(\frac{\partial q}{\partial t} - kq\right) \tag{48}$$

Noting that the exponential e^{-kt} appears with each term and can be factored out, the resulting equation of q contains the term -kq on both sides and these cancel, leaving the usual diffusion equation in q, but for a conservative mass ($k=0$).

Therefore, if a solution of the diffusion equation for a conservative substance, q(x,y,z,t), can be obtained, then the solution for concentrations of a substance which decays in the aquatic environment at a rate k is obtained simply as the product of the function q and the exponential e^{-kt}. This principle is assumed throughout much of this report in many discussions where the rate constant k is ignored for simplicity. Strictly speaking, this analogy only applies for instantaneous point source solutions since for solutions developed by superposition or integration, such as for continuous releases, the form of this exponential factor will change.

c. Conservation of Mass

Conservation of mass requires that the mass of a chemical substance in the receiving body, in the absence of any additional sinks or sources, remains constant. The total chemical mass in the water body is obtained as a function of time by the integral of the concentration over the entire volume of the transporting fluid:

$$M(t) = \int_V c(x,y,z,t)\, dV \tag{49}$$

Where additional sources (introduced by continuous releases) or sinks (associated with chemical degradation in the aquatic environment) are present, conservation of mass is re-stated slightly as: the total mass introduced into the transporting fluid, less the amount of that substance degraded by reaction, is equal to the total amount of substance being transported in the receiving fluid, as a function of time.

The principle of conservation of mass is applied to determine the value of constants in solutions of the diffusion equation for different types of fluid volumes. Also, since discharge rates, quantities, and degradation processes are relatively easy to quantify, under the imposed assumptions and constraints, conservation of mass principles using volume integrals can often be used to develop useful characterizations of the more complex concentration distribution behavior. In particular, application of volume integrals leads to simplified expressions which can be used to determine the average concentration within a region of interest as a function of time.

d. Remarks

In this abbreviated overview, the form of the diffusion equation as given in the discussion of molecular diffusion and turbulent dispersion may suggest that these types of motion are both governed by the same terms in the equation. This is not the case, although the form of the governing equation is the same [Equation (40)] for each type of motion in the absence of the other. For further information, reference[18] gives a brief but especially clear derivation of the form of the conservation equation containing both molecular diffusion and turbulent dispersion terms and shows the similarity in the governing equations that is observed if one process is neglected with respect to the other. Reference[73] gives a review of toxic spill modeling.

This subsection has given a brief and very simplified presentation of a complex topic to establish the basis from which the spill models have been developed. There are substantial and significant assumptions inherent in this formulation that are entirely beyond the scope of this report to even briefly describe. Isolated examples include the nature of chemical reactive processes, relative contributions of turbulent and molecular migration in different water body regions, water body stratification, thermal gradients, density gradients, and related effects of concentration gradients.

2. ONE-DIMENSIONAL DIFFUSION IN FLUID AT REST

In order to provide a basis for the characterization of the concentration distributions that are obtained from the more complex three-dimensional solutions of the diffusion equation under different boundary and initial conditions, the fundamental characteristics of these solutions are first described using simple one-dimensional illustrations. Where applicable, detailed definitions of functions or operations required for the evaluation of the three-dimensional solutions are also given.

One-dimensional diffusion, for example using x as the spatial coordinate, is associated with concentrations which are not dependent on the remaining spatial coordinates (y and z). This represents diffusion along the axis of a pipe or duct with uniform conditions across the section. Further assuming that the transporting fluid or receiving water body is at rest so that the velocity components of bulk fluid motion (u, v, w) are zero, then the governing partial differential equation becomes:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(e_x \frac{\partial c}{\partial x}\right) - kc \tag{50}$$

where the concentration c is to be obtained as a function of x, t, c(x,t), and the diffusion or dispersion coefficient, e_x, where the coefficient is assumed to be a constant. No distinction need be made at this stage as to whether the diffusion of a released mass in the fluid is molecular or turbulent in nature. The general form of the one-dimensional equation given above includes the reaction term, -kc, to account for decay of the diffusing mass in the transporting fluid.

3. INSTANTANEOUS SOURCES

a. Point Source

(1) General Solution

In the absence of decay (k=0), the well-known solution to the one-dimensional diffusion equation is given in the form:

$$c(x,t) = \frac{a}{\sqrt{t}}\, e^{-\frac{bx^2}{t}} \tag{51}$$

where a is a constant to be determined from conservation of mass.

Since

$$\frac{\partial^2 c}{\partial x^2} = \frac{2ab}{t^{3/2}} \left[\frac{2bx^2}{t} - 1 \right] e^{-\frac{bx^2}{t}} \text{, and} \tag{52}$$

$$\frac{\partial c}{\partial t} = \frac{a}{2t^{3/2}} \left[\frac{2bx^2}{t} - 1 \right] e^{-\frac{bx^2}{t}} \tag{53}$$

substitution into the diffusion equation (50) shows that the partial differential equation is satisfied for $b = \frac{1}{4\ e_x}$.

(2) Conservation of Mass

For one dimension, conservation of mass is written as a line integral along a volume having a constant unit cross section in the y-z plane to give for the total mass in the cross-sectional duct:

$$m = \int_{-\infty}^{\infty} c(x,t)\ dx = \int_{-\infty}^{\infty} \frac{a}{\sqrt{t}} e^{-\frac{x^2}{4e_x t}} dx \tag{54}$$

where the mass m is in lower case to signify mass per unit area. Evaluation of the integral using a transformation, $\xi = \frac{x}{2\sqrt{e_x t}}$, results in:

$$m = 2\ a \sqrt{e_x} \int_{-\infty}^{\infty} e^{-\xi^2} d\xi = \left(2\ a \sqrt{e_x} \right) (2) \left(\frac{\sqrt{\pi}}{2} \right) \tag{55}$$

The evaluation of the above integral utilizes the definition of the error function, erf(t), where:

$$\text{erf}(t) = \frac{2}{\sqrt{\pi}} \int_{0}^{t} e^{-\xi^2} d\xi \tag{56}$$

and corresponding limit values are erf(∞) = 1, erf(0) = 0. Additional information on the nature and computation of the error function is given in a following section.

The remaining constant in this one-dimensional solution of the diffusion equation can now be expressed in terms of the total mass in the system as:

$$a = \frac{m}{2\sqrt{e_x}\sqrt{\pi}} \tag{57}$$

where the total mass, m, of the chemical in the transporting fluid is taken to be time-invariant.

(3) Initial and Boundary Behavior

Substitution of the expressions for the constants a and b gives this one-dimensional solution in its final form, which can be written as:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2e_x t}}\, e^{-\frac{x^2}{4e_x t}} \tag{58}$$

Note that the exponential term x^2 indicates that the concentration distribution is symmetrical, in spatial coordinates, about the origin at x=0, and that the form of this distribution is Gaussian.

For large values of t, the concentration c(x,t) vanishes for all values of $|x|$, as it also does for very large values of $|x|$ if $t \neq 0$. The behavior in the limit as $t \to 0$ is such that the concentration is zero for all values of $|x| > 0$, but not at $x = 0$.

(a) Characterization of Instantaneous Point Source

At x=0, the concentration is obtained as a function of time in the form:

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MATHEMATICAL DEVELOPMENT OF THE SPILL ASSESSMENT MODEL (SAM) FO--ETC(U)
FEB 80 R G POTTS, J H HAGOPIAN, C R WOODRUFF F08635-79-C-0084
UNCLASSIFIED AFESC/ESL-TR-80-07 NL

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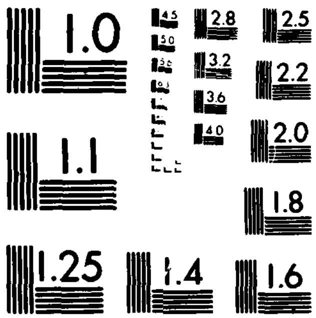
AD A
[illegible]



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$$c(o,t) = \frac{m}{\sqrt{2\pi}\sqrt{2e_x t}} \tag{59}$$

so that in the limit as t→0, the initial value of the concentration at the origin becomes infinitely large. Since, according to the principle of conservation of mass, the total mass in the fluid is constant and equal to m, the behavior of the concentration at the origin can be characterized as a fixed amount of mass being introduced into a volume (or length in the one-dimensional case) which becomes vanishingly small as t→0. The measure of this length is the term $\sqrt{2e_x t}$ appearing in the above equation and which is defined as the standard deviation of the Gaussian function, discussed in the next subsection.

Mathematically, the behavior of the concentration at the origin as t→0 becomes proportional to the Kronecka delta function and thus the description as an instantaneous (t=0) point (x=0) source applies.

This behavior of an infinitely large concentration at the origin in the limit as t→0, taken with the principle of conservation of mass, is a characteristic of the diffusion of a finite amount of substance introduced initially as a point source in an infinitely small volume of fluid at the origin, then spreading out to give a distribution of finite concentrations for non-zero values of time. Methods applicable to the integration of point source concentrations over a finite initial volume, for distributed sources, are discussed in a separate subsection of this report; since conservation of mass applies and the initial volume is taken at time t=0 to have a finite shape, the singularity is removed by these methods.

(4) Gaussian Distribution

The form of the concentration distribution, for t > 0, for this simplified one-dimentional example:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x t}}\ e^{-\frac{x^2}{4\ e_x t}} \tag{60}$$

is the Gaussian or normal curve having a maximum value, which decreases as time increases but remains located at the origin $x = 0$. Methods of developing solutions to the diffusion equation for substances in a moving fluid, such as a river, basically involve applying a linear coordinate transformation such that the Gaussian distribution, centered about the point of maximum value, is simply translated in the direction of the fluid flow with the same velocity as that flow.

The terms in the distribution given above are defined with the type of units of measure as:

$c(x,t)$ = concentration at a particular distance and time, in mass/volume
m = total dispersing mass, mass per unit area
x = distance
t = time
e_x = diffusion or dispersion coefficient, area/time

The x^2 term in the exponent shows that the distribution is symmetrical about the origin, that is, that

$$c(-x,t) = c(+x,t) \tag{61}$$

The variance of this distribution is given by $\sigma^2 = 2\, e_x t$ and the standard deviation, σ, or integral multiples such as 2σ, is used as a measure of the width of the distribution (or the spreading of the substance). In terms of the standard deviation, the one-dimensional concentration distribution is written as:

$$c(x,t) = \frac{m}{\sigma_x \sqrt{2\pi}}\, e^{-\frac{x^2}{2\,\sigma_x^2}} \qquad (62)$$

which is the more familiar form of the Gaussian curve. The standard deviation is a function of time given by $\sigma_x = \sqrt{2\, e_x t}$ and has units of length.

At the origin, x = 0, the value of the concentration c(0,t) depends on the reciprocal of the standard deviation, scaled by the constant terms m and $\sqrt{2\pi}$:

$$c(0,t) \cdot \frac{\sqrt{2\pi}}{m} = \frac{1}{\sigma_x} \qquad (63)$$

hence the behavior of $c(0,t) \to \infty$ as $t \to 0$.

For selected values of $\sigma_x = 1, 2,$ and 3, Figure 7 shows the resulting distributions over x. With each increase in σ_x, the maximum value at the origin decreases as $\frac{1}{\sigma_x}$ and the distribution spreads out over x.

(a) Distribution of Mass

The degree of spreading of the mass m can be determined by integrating with respect to the spatial coordinate x to give:

$$m(x,t) = \int_{-x}^{x} c(\xi,t)\, d\xi = \frac{m}{\sigma\sqrt{2\pi}} \int_{-x}^{x} e^{-\frac{\xi^2}{2\,\sigma^2}}\, d\xi \qquad (64)$$

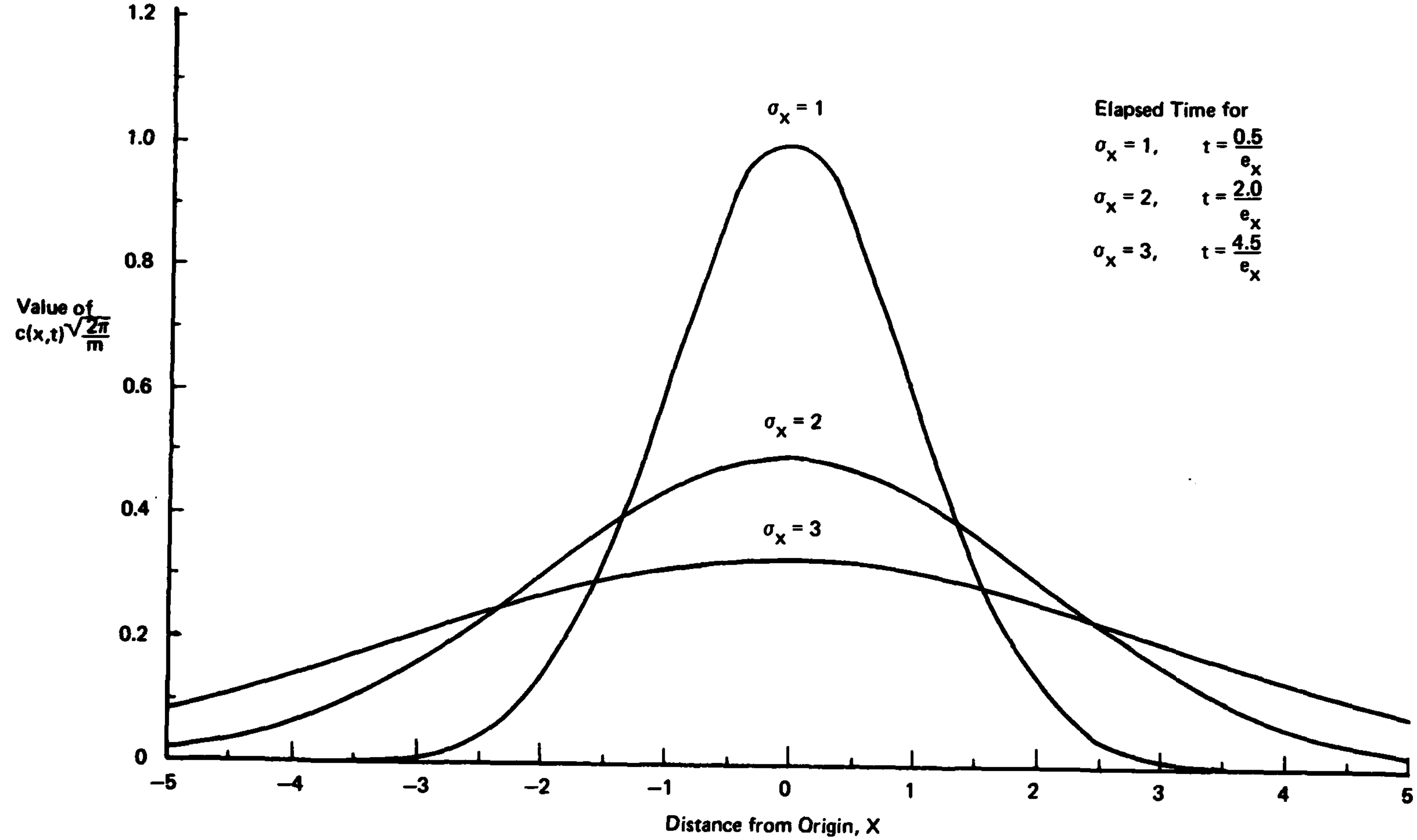


Figure 7. Gaussian Curves

where m(x,t) gives at time t the total amount of substance contained within the interval -x to +x. Evaluating the integral gives:

$$m(x,t) = m \cdot \operatorname{erf}\left(\frac{x}{\sigma\sqrt{2}}\right) \tag{65}$$

so that for $x = \sigma$, $m(\sigma,t)/m = .068$, and for $x = 2\sigma$, $m(2\sigma,t)/m = 0.95$. That is, for the latter example, at time t, 95 percent of the mass m is contained within an interval of width 4σ (since the interval is bounded by -2σ to $+2\sigma$). Sample illustrations are given in Figure 8 for several different values of σ.

Considering any multiple of the standard deviation as a characteristic length, expressed as $n\sigma$, the one-dimensional expression for the concentration can be written as:

$$c(x,t) = \frac{n \cdot m}{\sqrt{2\pi} \cdot n\sigma} e^{-\frac{x^2}{2\sigma^2}} \tag{66}$$

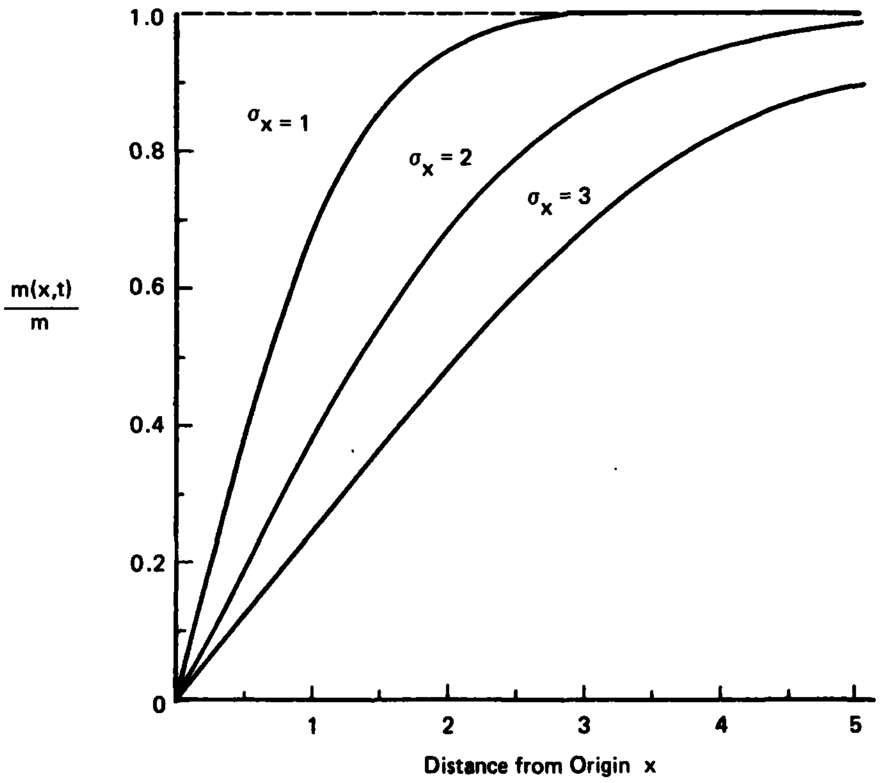
Since the characteristic length, $n\sigma$, appears in the demoninator, the behavior of $c(0,t) \to \infty$ at small values of times can be interpreted as an effect of the characteristic length having an initial value of 0.

(5) One-Dimensional Solution with Decay

If the mass m decays with a rate constant k, the solution for the one-dimensional instantaneous point source is given by:

$$c(x,t) = \frac{m}{\sigma_x\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma_x^2}} \cdot e^{-kt} \tag{67}$$

where the solution for a conservative mass ($k = 0$) is multiplied by a decay term, e^{-kt}, and $\sigma_x = \sqrt{2 e_x t}$. Differentiating with respect to x and t then



Curves show ratio of mass m(x,t) contained within interval −x to +x to the total mass in the system, m.

Figure 8. Mass Distribution

substituting into the partial differential equation for one-dimensional diffusion with decay shows that the equation is satisfied by this solution.

For conservation of mass, the mass integral:

$$m(x,t) = \int_{-x}^{x} c(\xi,t)\, d\xi = \frac{m}{\sigma_x \sqrt{2\pi}}\, e^{-kt} \int_{-x}^{x} e^{-\frac{\xi^2}{2\,\sigma_x^2}}\, d\xi \tag{68}$$

is evaluated as earlier to give:

$$m(x,t) = m\, e^{-kt}\, \mathrm{erf}\left(\frac{x}{\sigma\sqrt{2}}\right) \tag{69}$$

In the limit as x→∞ the value of the error function approaches 1 so the total quantity of dispersing mass is given as a function of time by $m \cdot e^{-kt}$.

(6) Behavior of Instantaneous Point Source Solution

The concentration estimated by the instantaneous point source solution (for one dimension) of

$$c(x,t) = \frac{m}{\sigma_x\sqrt{2\pi}}\, e^{-\frac{x^2}{2\,\sigma_x^2}} \tag{70}$$

corresponds to a distribution of the constant mass m in time and space of

$$m(x,t) = m \cdot \mathrm{erf}\left(\frac{x}{\sigma\sqrt{2}}\right) \tag{71}$$

where $\sigma_x = \sqrt{2\, e_x t}$. As both x and t become large, the concentrations c(x,t) approach zero, and earlier subsections showed that, for $t = 0$, the concentration is zero for all x except at the origin where the initial concentration is infinitely large. This subsection summarizes some additional expressions useful for characterizing the nature of the concentration and mass distributions between these limits.

(a) Time History at the Origin ($x = 0$)

Since for any value of time, the location of maximum concentration along the line occurs at the origin, $x = 0$, then the time history at the origin can be used to determine the total elapsed time during which concentrations above a specified limit can be expected to exist anywhere in the environment.

The concentration at the origin is given as a function of time by:

$$c(0,t) = \frac{m}{\sigma_x \sqrt{2\pi}} = \frac{m}{2\sqrt{\pi}\sqrt{e_x t}} \tag{72}$$

and as t ranges from 0 to ∞, the concentration ranges from ∞ to 0. The time at which a specified concentration occurs at the origin is simply obtained as:

$$t = \frac{m^2}{4\pi\, e_x\, c^2(0,t)} \tag{73}$$

The elapsed time required for the concentration at the origin to be reduced from the initial infinite value to the density, ρ, of the spilled chemical is denoted as t_ρ and is obtained by substituting $c(0,t) = \rho$:

$$t_\rho = \frac{m^2}{4\pi\, e_x\, \rho^2} \tag{74}$$

At this value of time, the chemical mass will have dispersed according to

$$m(x,t_\rho) = m \cdot \mathrm{erf}\left(\frac{x}{2\sqrt{e_x\ t_\rho}}\right) \tag{75}$$

but 95 percent of the mass will be contained within a distance of $x = \pm\ 2.772\sqrt{e_x\ t_\rho}$. Substituting for t_ρ gives, in terms of the density of the chemical,

$$x = \pm \frac{1.386}{\sqrt{\pi}} \frac{m}{\rho} = \pm\ 0.782\ \frac{m}{\rho} \tag{76}$$

which gives the width of the 95 percent distribution as $1.564\ \frac{m}{\rho}$ for which the concentration at the origin is equal to the density. If the entire mass were initially distributed about the origin at a constant concentration equal to the density then the width of the distribution would be $\frac{m}{\rho}$; the Gaussian solution gives for the fraction of mass contained within this interval at time t_ρ:

$$\frac{m\left(\frac{m}{2\rho},\ t_\rho\right)}{m} = \mathrm{erf}\left(\frac{\sqrt{\pi}}{2}\right) = 0.79 \tag{77}$$

Thus, at the elapsed time for which the concentration at the origin is reduced to a value equal to the density, the Gaussian distribution still retains 79 percent of the mass within an interval that would correspond to an initial distributed discharge of m at a constant concentration equal to the density (ρ) of the chemical.

At any time t, the concentration distribution has a maximum value at the origin, with decreasing values for all $|x| > 0$. If a lower limit can be specified for the concentration, C_L, such that concentrations less than C_L are not considered hazardous, then the maximum duration for which concentrations at any point in the environment may exceed C_L is given by the elapsed time for the concentration at the origin to reach C_L. This value of elapsed time, denoted at t_L, is given by:

$$t_L = \frac{m^2}{4\pi\, e_x\, C_L^2} \tag{78}$$

(b) Time History at Point x

Since the concentrations at all values of $|x| > 0$ are initially zero and are zero for very large values of time, at any point x, at some time after the spill occurs, the concentration observed increases to a maximum value, then decreases as further dispersion takes place. The maximum concentration, at a fixed value of x, occurs when $\frac{\partial c}{\partial t} = 0$ which for Equation (60) is

$$t_{max} = \frac{x^2}{2\, e_x} \quad , \qquad \text{or} \qquad e_x\, t_{max} = 0.5\, x^2 \tag{79}$$

The concentration at this time and location is determined by substituting into Equation (60):

$$c(x, t_{max}) = \frac{m\, e^{-1/2}}{\sqrt{2\pi}} \cdot \frac{1}{x} = 0.24197\, \frac{m}{x} \tag{80}$$

These two expressions together define coordinates along the envelope of maximum concentration as a function of x, giving the maximum concentration at a location and the time at which it occurs.

Figure 9 gives an illustrative plot of the values of the peak concentration (expressed as $c(x,t_{max})/m$) and the arrival time (expressed as $e_x\, t_{max}$) as a function of distance from the origin of the spill. This indicates, for example,

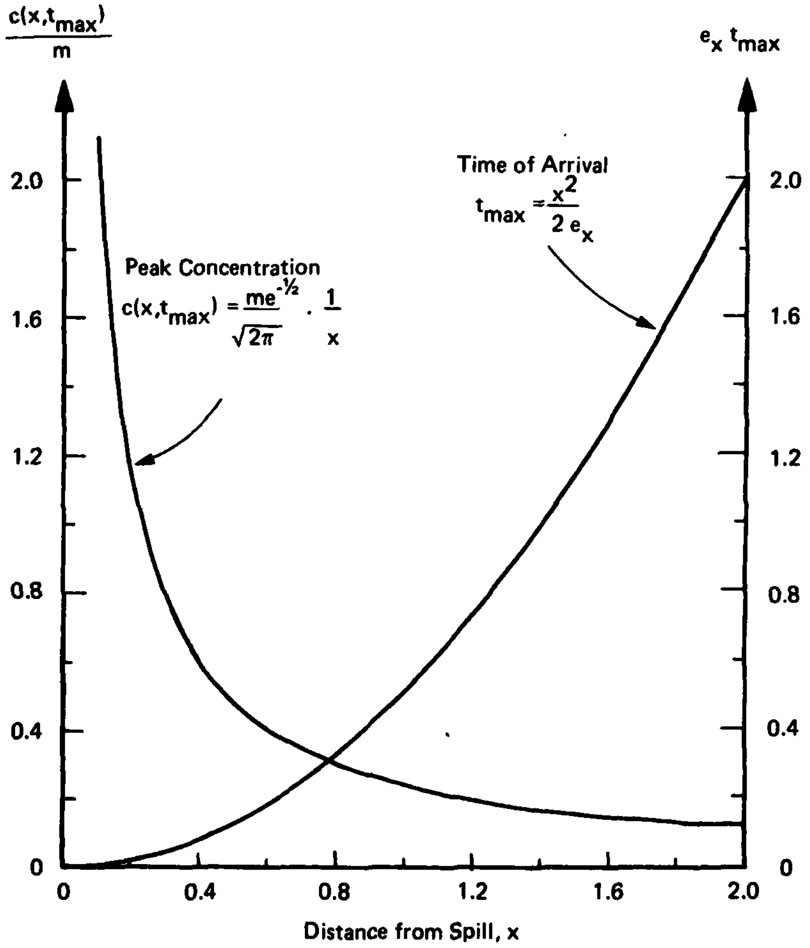


Figure 9. Concentration Envelope Versus Distance

that the peak concentration at a distance x = 0.5 is approximately 0.48 meter, and the concentration reaches that value at this location at a time of $\frac{0.125}{e_x}$ as shown in Figure 9.

Near the spill site, very large concentrations occur at short times after the start of the spill. Very far from the spill site, the peak concentrations reach only small values at long times after the spill has occurred. Limits on expected concentrations can be used to estimate the times and distances over which concentrations of interest will exist and thus determine bounds on time and distance scales.

The expression for the maximum concentration at x, Equation (80), is readily rearranged to determine the maximum distance from the spill location at which concentrations of any specified value will exist:

$$x = \frac{m\, e^{-\frac{1}{2}}}{\sqrt{2\pi}} \frac{1}{c(x, t_{max})} \tag{81}$$

The time at which the concentration reaches this value at x is given by $t_{max} = \frac{x^2}{(2\, e_x)}$, so that the upper limits on the values of x and t are determined if $c(x, t_{max})$ is given as the minimum concentration of interest.

Near the spill site the peak concentrations will exceed the density of the spilled chemical. The coordinates on the envelope corresponding to a concentration equal to the chemical density can be obtained in terms of the density as:

$$x = \frac{m}{\sqrt{2\pi e}} \cdot \frac{1}{\rho} \tag{82}$$

where the numerical value of e is not to be confused with e_x, and

$$t_{max} = \frac{m^2}{4\pi e \cdot e_x \rho^2} \tag{83}$$

At distances greater than this value of x, the concentration will not exceed the density at any elapsed time greater than zero. At locations closer to the spill point than this value of x, the concentration will be greater than the density from time t = 0 to an elapsed time less than the value of t_{max} given above.

Since at any location x the concentration increases with elapsed time from the start of the spill to a maximum value, then gradually decreases, the time history of the concentration at a particular point is of interest as is the length of time at that location for which a given concentration level will be exceeded. The concentration at any point x is determined by substituting Equation (79) into Equation (60):

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\, e_x t}}\, e^{-\frac{x^2}{4\, e_x t}} = \frac{1}{2\sqrt{\pi}}\,\frac{m}{\sqrt{e_x}}\,\frac{1}{\sqrt{t}}\, e^{-\frac{t_{max}}{2t}} \tag{84}$$

and this distribution is illustrated graphically in Figure 10. Initially the concentration rises rapidly from zero (for $|x| > 0$) to the maximum value, then, for larger times, is reduced more gradually until returning to zero for large values of elapsed time. For small values of time, the argument of the exponential $\left(\frac{t_{max}}{2t}\right)$ is large since t varies from zero to t_{max}, and the concentration profile is strongly influenced by an exponential rise from the value of 0 to the maximum value. For times greater than t_{max}, the argument of the exponential is increasingly reduced so that the exponential term approaches its limiting value of 1.0 asymptotically, and the reduction of concentration for times greater than t_{max} closely follows the behavior of

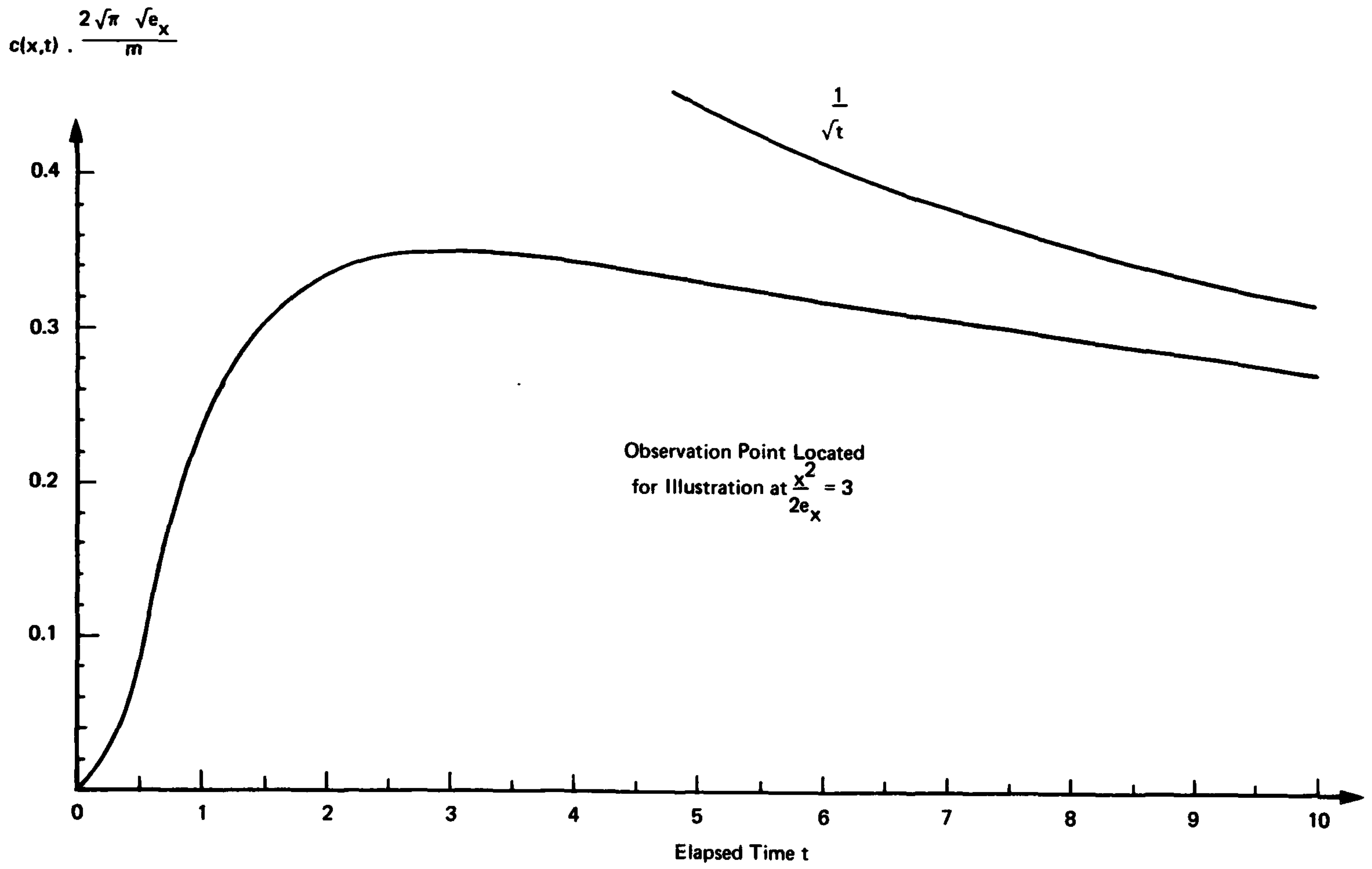


Figure 10. Concentration Time History at Location X

$\frac{1}{\sqrt{t}}$.

The time of arrival and duration at a specific observation point of concentrations in excess of a specified value are not readily obtained in a closed form solution; however, this information can be interpolated from graphical displays of the concentration time history at the observation point.

(c) Extent of Hazard

By inverting Equation (70) for concentration, the distance at which a specified concentration exists at any aprticular time can be obtained:

$$x^2 = 2\,\sigma_x^2 \ln\left[\frac{m}{\sqrt{2\pi}\,\sigma_x\,c(x,t)}\right] = 4\,e_x t \ln\left[\frac{m}{2\,c(x,t)\sqrt{\pi\,e_x t}}\right] \tag{85}$$

Figure 11 illustrates the type of profiles produced from this equation by setting c(x,t) to a particular hazard level and then computing values of distance x over a range of elapsed times. The peak of the hazard profile shown in Figure 11 corresponds graphically to the maximum value of $\frac{x}{\sqrt{2\,e_x}}$ over which the particular hazard level will exist. For distances less than this maximum hazard extent, the profile shown in Figure 11 can be used to obtain the elapsed times during which the concentration at a particular distance will exceed the particular hazard level.

The maximum distance reached by the hazardous concentration is obtained from Equation (80) as:

$$x^2 = \frac{m^2}{2\,c^2(x,t)\,\pi\,e} \qquad (e = 2.718\ \ldots) \tag{86}$$

and the time at which this distance is reached is obtained from:

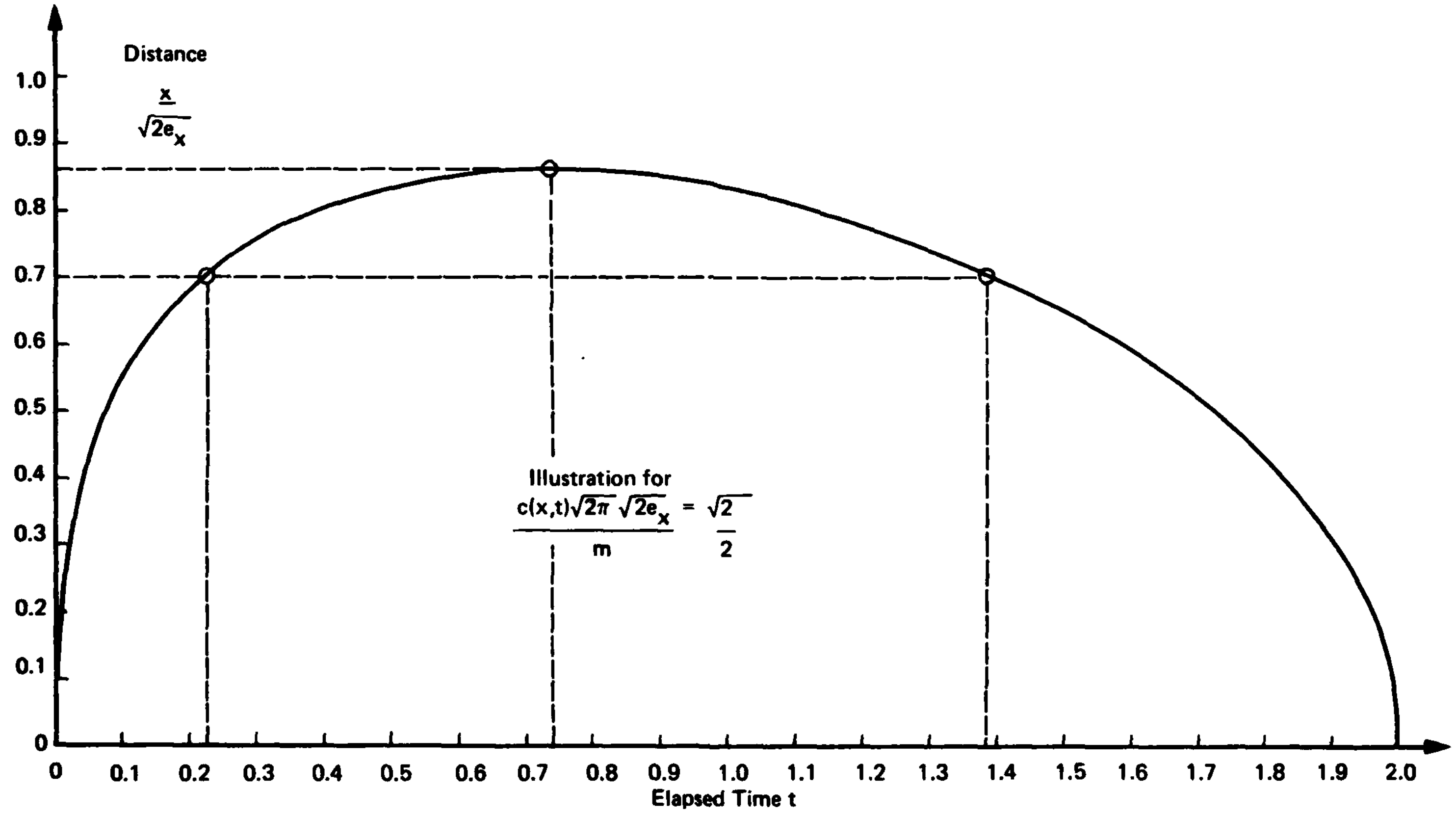


Figure 11. Hazard Extent as a Function of Time

$$t = \frac{m^2}{4\ c^2(x,t)\ \pi\ e_x \cdot e} \tag{87}$$

Since the concentration c(x,t) is the maximum value reached at that location x, over time, the relation $t = \frac{x^2}{(2\ e_x)}$ is also satisfied.

For large values of time, the chemical mass will continue to spread until the concentration everywhere along the line is reduced to values less than the specified concentration. The point at which this occurs is determined, from the time history at the origin, when c(0,t) is equal to c(x,t). This gives the maximum elapsed time for this profile in terms of the specified concentration as:

$$t^* = \frac{m^2}{4\ \pi\ e_x\ c^2(x,t)} \tag{88}$$

where t* is the time of distribution for location x to experience a concentration more than c(x,t). Substitution of this value in the expression [Equation (85)] for distance as a function of time and concentration shows that the argument of the logarithm goes to one, giving a distance x = 0. Since the concentration at this origin is always a maximum, concentrations greater than a specified concentration cannot exist beyond the time that the concentration at the origin reaches this value.

For very small values of time, the argument of the logarithm becomes infinitely large, with possible attendant numerical difficulties; however, in the limit as $t \rightarrow 0$, the value of x also approaches zero.

Plotted displays of the hazard extent profiles, prepared for a specific hazardous concentration level, give the total time during which the concentrations in the environment exceed the hazard level, the maximum distance for which this occurs and, for smaller distances, the time period during which that level is exceeded.

(d) Computation of Arrival Times and Durations

Given the expression for concentration as a function of time and distance, if the time a specified concentration occurs at a given location is desired, the equation can be transformed but the required values of time appear as the roots of a transcendental function. Numercial methods can be applied to obtain solutions, and techniques such as Newton's method are efficient, given appropriate starting values.

Since the maximum concentration and time of occurrence, t_{max}, can be computed for any location x, the arrival times exist at x only for specified concentrations less than the maximum value. This leads to a further condition that one root, t_1, of the transcendental function must be in the range $0 < t_1 < t_{max}$ while the other root t_2 must be greater than t_{max}. In some cases, writing the transcendental equation in terms of the specified concentration, and the maximum concentration at the value of x, an expression can be obtained in which the time-dependent terms are isolated. Since the form of the transcendental expressions involving time are then independent of any particular spill conditions, further investigation of this topic could produce very useful results if a direct numerical representation of the inverse transcendental function could be developed.

Since other types of concentration profiles can be used for graphical interpolation of this information, and, since the iterative approach used for standard numerical solutions would require substantial additional computations, solutions to these types of transcendental functions have not yet been incorporated in the spill model.

(e) Behavior for Non-Conservative Chemical

Where decay or degradation of the chemical in the environment is assumed to occur, the reduction of the dispersing mass takes place exponentially, as determined by the value assumed for the rate constant, k. Equivalent expressions for the behavior of the one-dimensional instantaneous point source solutions are briefly summarized in the following paragraphs.

The time history of the concentration at the origin is given by:

$$c(0,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x t}}\ e^{-kt} \tag{89}$$

which gives the concentration as a function of both elapsed time, and the total amount of mass in the environment which is also a function of time: $m\ e^{-kt}$. As a result of the introduction of the exponential decay term, this expression is not readily inverted to yield an equation for elapsed time, t, in terms of the concentration c(0,t). The substitution $c(0,t) = q(0,t)\ e^{-kt}$ yields an equation in which time can be expressed as a function of q(0,t) so that a first approximation can be made by solving for the time at which q(0,t) reaches the values of c(0,t); the actual time at which the concentration reaches the value c(0,t) will be less since the decay has, in effect, been ignored.

At any location x, the maximum concentration occurs when $\frac{\partial c}{\partial t} = 0$ which leads to:

$$\frac{1}{t_{max}} = \frac{e_x}{x^2} + \frac{e_x}{x^2}\sqrt{1 + \frac{4\ x^2\ k}{e_x}} \tag{90}$$

and the concentration at that time and location is obtained by substitution of this value in the equation for $c(x,t)$.

The time history of the concentration at a location x is given by:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\, e_x t}}\, e^{-\frac{x^2}{4\, e_x t}}\, e^{-kt} \qquad (91)$$

The distance at which a specified concentration exists at any particular time is obtained as:

$$x^2 = 4\, e_x t \ln\left[\frac{m}{2\, c(x,t)\sqrt{\pi\, e_x t}}\right] - 4\, e_x\, kt^2 \qquad (92)$$

For values of $t > 0$, this expression is zero for

$$\sqrt{t}\, e^{kt} = \frac{m}{2\, c(x,t)\sqrt{\pi\, e_x}} \qquad (93)$$

By analogy to the case where $k = 0$, this distance x is zero when the concentration at the origin $c(0,t)$ has decayed to a value equal to $c(x,t)$, and the time history at the origin can be used to determine the time range for the computation of maximum hazard distances for any particular concentration. The maximum distance over which concentrations exceeding the specified level is obtained by substituting the value of t_{max} into the expression for x^2.

(7) Error Function

(a) Definition

The error function, written as $\mathrm{erf}(x)$, commonly appears in solutions developed from the diffusion equation and is defined as:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} \, dt \tag{94}$$

Since the error function gives an integral of the Gaussian or normal distribution, further information is usually found in standard reference texts on probability and statistics. A particularly detailed analytical study, pre-dating widespread use of computers, is given by Rosser[21], and Ng and Geller[22,23] have compiled especially useful tables of integrals of the error function. The following subsection is limited to a brief description of the form of the function, its behavior, and a method of numerical evaluation.

(b) Characteristics

Since the error function of x is defined by the integral from 0 to x for negative values of x, it follows that:

$$\mathrm{erf}(-|x|) = \frac{2}{\sqrt{\pi}} \int_{0}^{-|x|} e^{-t^2} \, dt \tag{95}$$

and using the transformation $\beta = -t$, that

$$\mathrm{erf}(-|x|) = -\frac{2}{\sqrt{\pi}} \int_{0}^{-|x|} e^{-\beta^2} \, d\beta = -\mathrm{erf}(|x|). \tag{96}$$

Thus, the error function for negative values of x is a mirror image of the function for positive values, in the form $\mathrm{erf}(-x) = -\mathrm{erf}(x)$. The value of the function at $x = 0$ is 0, and values for $x > 0$ are illustrated in Figure 12. As can be seen from the figure, the value of the error function

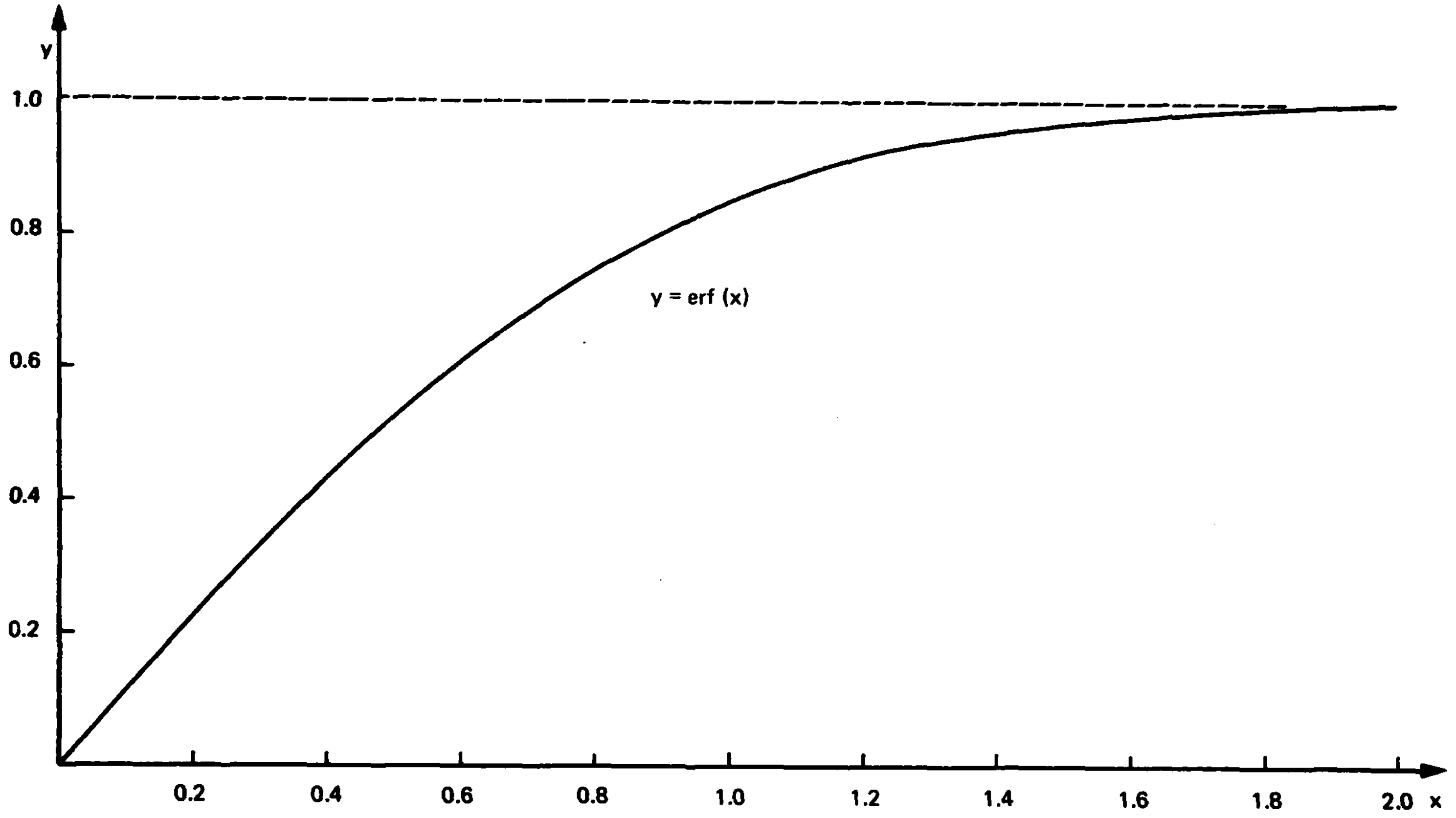


Figure 12. Error Function

rises very rapidly, over a short range of x, to a value asymptotically approaching 1.0. At x = 2.0, for example, the value of the error function is approximately 0.995.

Since

$$\int_0^\infty e^{-t^2}\,dt = \frac{\sqrt{\pi}}{2} \tag{97}$$

it can be seen that

$$\lim_{x\to\infty} [\mathrm{erf}(x)] = +1 \tag{98}$$

and

$$\lim_{x\to\infty} [\mathrm{erf}(-|x|)] = -1 \tag{99}$$

(c) Approximations

(i) For large values of the error function argument, an asymptotic expansion is used to obtain:

$$\sqrt{\pi}\, x\, e^{x^2}\,(1 - \mathrm{erf}(x)) \sim 1 + \sum_{m=1}^{\infty} (-1)^m \frac{1\cdot 3 \cdots (2m-1)}{(2x^2)^m} \tag{100}$$

In the limit as x becomes large,

$$\lim_{x\to\infty} [\sqrt{\pi}\, x\, e^{x^2}\,(1 - \mathrm{erf}(x))] = 1 \tag{101}$$

which reduces to an approximation for the error function behavior at large values of the argument:

$$\mathrm{erf}(x) = 1 - \frac{e^{-x^2}}{\sqrt{\pi}\,x} \quad , \; x \to \infty \tag{102}$$

(ii) For error function arguments very close to 1, an approximation for the value of the error function can be obtained by writing

$$\mathrm{erf}(x) = \mathrm{erf}(1 + \delta) = \frac{2}{\sqrt{\pi}} \int_0^{1+\delta} e^{-t^2}\, dt \tag{103}$$

then introducing the approximation to give:

$$\mathrm{erf}(1 + \delta) = \frac{2}{\sqrt{\pi}} \int_0^{1} e^{-t^2}\, dt + \frac{2}{\sqrt{\pi}}\, e^{-1} \int_1^{1+\delta} dt \tag{104}$$

which reduces to:

$$\mathrm{erf}(1 + \delta) = \mathrm{erf}(1) + \frac{2\delta}{e\sqrt{\pi}} \; , \; \delta << 1 \tag{105}$$

where erf(1) is approximately 0.8427.

(iii) The same approximation may be used to write for very small arguments of the error function:

$$\mathrm{erf}(\delta) = \frac{2}{\sqrt{\pi}} \int_0^{\delta} e^{-t^2}\, dt \sim \frac{2}{\sqrt{\pi}} \int_0^{\delta} dt \tag{106}$$

which gives

$$\mathrm{erf}(\delta) \sim \frac{2\delta}{\sqrt{\pi}} \qquad \text{for } \delta \to 0. \tag{107}$$

(d) Numerical Evaluation

Since erf(-x) = -erf(x), one can write for erf(x) in the range $-\infty < x < \infty$:

$$\mathrm{erf}(x) = -\frac{2}{\sqrt{\pi}} \int_0^{|x|} e^{-t^2}\, dt, \quad -\infty < x \leq 0 \tag{108}$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^{x} e^{-t^2}\, dt, \quad 0 \leq x < \infty \tag{109}$$

Hastings' [24] approximation gives for the error function written as:

$$\mathrm{erf}(x) = \phi(x) = \frac{2}{\sqrt{\pi}} \int_0^{x} e^{-t^2}\, dt, \quad 0 \leq x < \infty \tag{110}$$

the numerical approximation in the form:

$$\phi^*(x) = 1 - (a_1\eta + a_2\eta^2 + a_3\eta^3 + a_4\eta^4 + a_5\eta^5)\ \phi'(x) \tag{111}$$

where

$\phi'(x)$ is the value of the error function integrand evaluated at x, and

$\phi^*(x)$ is used to signify the numerical approximation to $\phi(x)$ [= erf(x)].

The variable η is defined as:

$$\eta = \frac{1}{1 + p\,x} \tag{112}$$

where the value of the coefficient p is given by Hastings as $p = 0.3275911$. The value of η ranges from 1 at $x = 0$ to 0 as $x \to \infty$.

Since

$$\phi'(x) = \frac{2}{\sqrt{\pi}}\, e^{-x^2} \tag{113}$$

the values of the coefficients a_1 to a_5 in the approximation may be pre-multiplied by the constant $\frac{2}{\sqrt{\pi}}$ to give transformed coefficients $b_1 = \frac{2}{\sqrt{\pi}} a_1$, and so forth, reducing the approximation to:

$$\phi^*(x) = 1 - (b_1\eta + b_2\eta^2 + b_3\eta^3 + b_4\eta^4 + b_5\eta^5)\; e^{-x^2} \tag{114}$$

Finally, for numerical efficiency the approximation can be written in the form:

$$\phi^*(x) = 1 - \eta\;(b_1 + \eta\;(b_2 + \eta\;(b_3 + \eta\;(b_4 + \eta\; b_5))))\; e^{-x^2} \tag{115}$$

for the range $0 \leq x < \infty$.

For negative arguments (values of x), the same form of the approximation can be applied by using:

$$\phi^*(x) = -\phi^*(|x|) \ , \text{ for } x < 0. \tag{116}$$

Using the values of the coefficients a_1 to a_5 as tabulated by Hastings, pre-multiplying by the factor $\frac{2}{\sqrt{\pi}}$ produces the values of the scaled coefficients as:

$$\begin{aligned} b_1 &= +0.2548\ 2959\ 2 \\ b_2 &= -0.2844\ 9673\ 6 \\ b_3 &= +1.4214\ 1374\ 1 \\ b_4 &= -1.4531\ 5202\ 7 \\ b_5 &= +1.0614\ 0542\ 9 \end{aligned} \tag{117}$$

At the origin, x=0, the variable η=1 and the approximation to the error function reduces to:

$$\phi^*(x=0) = 1 - (b_1 + b_2 + b_3 + b_4 + b_5) = 0 \tag{118}$$

from which the condition is obtained that

$$\sum_{i=1}^{5} b_i = 1.0 \tag{119}$$

For the values of the coefficients tabulated above, the sum of the coefficient values is obtained as 0.9999 9999 9.

Finally, the maximum value on the error curve given by Hastings for the approximation is 1.5×10^{-7}. For large values of x, the function should approach a value of 1, and the term (1 - erf(x)), for large x, should approach zero. When used in dispersion equations, this term appears as a product in expressions also containing terms becoming increasingly large as x increases. In practice, the different accuracies and rates of convergence of numerical approximations can lead to unstable products deviating from the asymptotic limit of 0. These effects can be compensated for, in part, in the computation of the error function value, by setting the function value to 1 when that limit is reached within the accuracy of the numerical approximation. That is, if $|1.0 - \mathrm{erf}(x)| < 1.5 \times 10^{-7}$, then erf(x) is taken to be exactly 1.0.

(e) Alternate Formulations

(i) Frequently as noted above the error function terms appear in solutions of the diffusion equation in the form 1-erf(x) which is the complementary function to the error function and is written as erfc(x). For values of $x > 0$, Hastings approximation for erf(x) can be modified slightly to obtain a direct approximation to erfc(x) in the form:

$$\mathrm{erfc}(x) = 1-\mathrm{erf}(x)$$

$$= \eta\ (b_1 + \eta\ (b_2 + \eta\ (b_3 + \eta\ (b_4 + \eta\ b_5))))\ e^{-x^2} \qquad (120)$$

To simplify the notation, the polynomial can be written as $P(b,\eta)$ so that the approximations become:

$$\mathrm{erf}(x) = 1 - P(b,\eta)\, e^{-x^2}, \quad x \geq 0 \tag{121}$$

$$\mathrm{erfc}(x) = P(b,\eta)\, e^{-x^2}, \quad x \geq 0 \tag{122}$$

A particular advantage of the form of the expression for the approximation to erfc(x) is that a decaying exponential term is isolated as a factor of the approximation. This term then becomes available for combination with increasing exponential terms which, for certain conditions, appear in solutions to the diffusion equations, and operates to alleviate numerical instabilities associated with computations in the form $e^{x_1} \cdot e^{-x_2}$ in the limit as both x_1 and x_2 become large.

At $x=0$, the variable $\eta=1$ and the polynomial

$$P(b,1) = \sum_{i=1}^{5} b_i = 1 \tag{123}$$

and for large values of x, $\eta \to 0$ and

$$P(b,0) = 0. \tag{124}$$

In the limit as x becomes large, compensation for the maximum value in the error of the computation of the error function is applied such that if $|P(b,\eta)| < 1.5 \times 10^{-7}$, then $P(b,\eta)$ is taken as exactly 0.0 to give the limit value for erfc(x) as $x \to \infty$. Note that this assumes the exponential term has been factored out, since the limit condition is more correctly applied to erfc(x).

For negative values of x,

$$\mathrm{erfc}(x) = \mathrm{erfc}(-|x|) = 1 - \mathrm{erf}(-|x|) \tag{125}$$

so that

$$\mathrm{erfc}(x) = 1 + \mathrm{erf}(|x|) \ , \quad x < 0 \tag{126}$$

and the substitution of the approximation produces the result:

$$\mathrm{erfc}(x) = 2 - P(b,\eta)\ e^{-x^2} \tag{127}$$

where $x < 0$ and η is evaluated for $|x|$.

(ii) Although the value of the error function is limited, $|\mathrm{erf}(x)| \leq 1.0$, for all values of the argument $-\infty \leq x \leq \infty$, difficulties can arise in the computation and representation of the argument value, particularly if the function value is required in the form:

$$z = \mathrm{erf}\left(\frac{x_1}{x_2}\right) \tag{128}$$

and in the limit cases $x_1 \to \infty$ or $x_2 \to 0$.

Thus, an alternate form of the error function computation can be used, first examining the values of x_1 and x_2 then setting the value of the error function as follows:

$$\lim_{x_2 \to 0} \mathrm{erf}\left(\left|\frac{x_1}{x_2}\right|\right) = 1, \quad x_1 >> x_2 \tag{129}$$

$$\lim_{x_1 \to 0} \operatorname{erf}\left(\left|\frac{x_1}{x_2}\right|\right) = 0, \quad x_2 >> x_1 \tag{130}$$

Limit values in the event both x_1 and x_2 become very large or very small can also be set but depend on the rate at which each approaches the limit. Where the ratio x_1/x_2 is finite, the usual form of the approximation is used.

(8) Limits of Numerical Representation

For use in computations, numerical values are represented and manipulated on computer systems in a variety of forms depending on the type of value and the architecture and word structure of the computer system. Since these numerical representations have finite limits, in turn, limits are implied on the range of computations that can be performed using these values. The most significant effects of these limits on computations arising in the use of the spill models are briefly summarized below. Reference is made to manufacturers' publications[25] for complete information regarding the details of representation and storage of different types of numerical values; examples below are illustrated using limits appropriate to the CDC 6600 series computer.

Real, single precision data constants or values are written using scientific notation as in $\pm$ n.nE $\pm$ S where the coefficient or base, indicated as n.n, is multiplied by a power of 10, as indicated by E±S which denotes $10^{\pm S}$. This notation corresponds to the internal representation with separate provision made for the sign, coefficient and exponent. In external or printed form the value of the exponent depends on the magnitude of the number and on the location of the printed decimal point; for internal use, storage conventions are standardized using normalized coefficients (e.g., $\pm$ 0.nn...) so that the value of the exponent depends only on the magnitude of the number.

Since the CDC 6600 has a large word length, the number of decimal digits that can be carried for the coefficient of a real number is also quite large (approximately 14). Other machines commonly used for scientific computation typically have smaller word lengths and correspondingly reduced precision in the number of digits that can be carried. For increased accuracy, real values can be stored in more than one computer word (for example, as in double precision); under most schemes of storage this increases the number of digits that can be represented but not necessarily the range of the magnitude of the value.

For the CDC 6600, limit values of a real constant or variable are stated as +0, -0 or as having a magnitude in the range 10^{-293} to 10^{+322}; the ± 0 values arise as special cases in the representation of exponent values. Use of constants or variables which have values near these limits or combine in such a way that resulting computations may be required to exceed these limits will lead to overflow or underflow conditions. The results of subsequent computations may not always be predictable, and since the computer system response and/or recovery is dependent on the system architecture and software, automatic recovery procedures may not, in general, be as desired (e.g., run termination), nor consistent among machines of different manufacture.

Since the physical processes corrresponding to the spill model lead to interest in behavior at limit conditions, such as the time history of the concentration at the location of a spill or the maximum distance over which a concentration at a specified level may exist, the equations employed may be required to perform computations, at or near these limits, which are highly susceptible to overflow or underflow conditions. Thus, for selected use in these computations, and for assisting in establishing allowable ranges for user specified variables, inclusion of a generalized method of detecting and recovering from the use of very large or very small numerical values is desirable.

The allowable magnitude (absolute value) of a real variable can be monitored by specifying the values of two exponential limits in parametric form, a and b, such that the value of any real variable x can be constrained to be within the precision of the computer by:

$$x = 0 \tag{131}$$

or

$$|x| > 10^{-a}$$

$$|x| < 10^{+b} \tag{132}$$

For each computer, the values of a and b depend on the characteristics of floating point or real value storage and therefore are machine dependent parameters within the spill model. The use of these limits to test and control values of individual variables is not always feasible, and the principal application lies in their use to determine the maximum allowable range for a dependent variable, given a pre-specified range of an independent variable.

(a) Exponential Function

The computation of the value of the function $x = e^y$ is subject both to limitations in the accuracy of the numerical approximation employed for the form of the exponential and in the limiting value, x, of the function that can be returned as governed by the internal representation for storage of the computed value on the particular computer system. Unfortunately, in this case, in common use the argument of the function is usually tested before the computation is attempted, resulting in an automatic error condition or termination if the computed value would exceed the storage limits.

For the CDC 6600, the allowable arguments or values of y are defined to be in the range:

$$-675.84 \leq y \leq 741.67 \tag{133}$$

Since the magnitude of the computed result is constrained, for the CDC 6600, as:

$$10^{-293} \leq |x| \leq 10^{+322} , \tag{134}$$

the limit values for the exponential function argument can be seen to result from:

$$10^{-293} \leq e^y \leq 10^{+322} \tag{135}$$

or

$$-293 \ln_e 10 \leq y \leq 322 \ln_e 10 \qquad (136)$$

The limiting value parameters, a and b, are especially useful to provide for overriding overflow/underflow detection and response in machine-dependent computations by setting values of exponential function as follows:

$$e^y = 0, \quad \text{if} \quad y < (-a) \ln_e 10$$

$$e^y = 10^b, \quad \text{if} \quad y > (b) \ln_e 10 \qquad (137)$$

For cases in which the exponential function argument is itself a function of several variables, these limits can also be applied to infer ranges of values of dependent combinations of these variables for which, given a prespecified range of an independent variable, values obtained for the exponential function will be defined.

It should also be noted that as usually formulated, the argument of the exponential function is normally dimensionless, so that changing the units of measure of individual terms will not substantially affect the limit at which the function computation fails. However, when the argument is obtained as a function of several other variables, the units of measure may have an effect if the computations to obtain the argument are performed so that intermediate results do depend on physical units. An example is the computation of the argument for $e^{-\frac{x^2}{2\,\sigma^2}}$ where $\frac{x^2}{2\,\sigma^2}$ is non-dimensional and may be evaluated by $\frac{1}{2} \cdot \frac{x}{\sigma} \cdot \frac{x}{\sigma}$ or $\frac{(x \cdot x)}{(2 \cdot \sigma \cdot \sigma)}$. In the latter expression, the units in which x and σ are given could affect the computation since the dimensional quantities x^2 and σ^2 are formed first.

(b) Other Functions

In addition to limitations arising from numerical representations as described above, other limit conditions which are present include those associated with the definitions of mathematical functions such as the square root, for which a real result is defined only if the argument is greater than, or equal to, zero. For this example, in cases where an argument value is determined by a series of computations, it is possible that very near the limiting value of zero the series of computations may yield a very small negative number even though analytically the limit value may appear to be approached correctly. Therefore, where computations are expected to be performed in a general manner using values derived from user specifications under limited constraints, special tests for limit conditions applicable to arithmetic functions are required to avoid interruption or failure of these computations.

b. Distributed Source

With an instantaneous point source, the solution to the diffusion equation gives a distribution over time and space of a finite mass that is in effect initially concentrated in an infinitely small volume at the spill origin. These solutions then have a drawback in that infinite concentrations are obtained initially at the spill location, and for some time, and distance close to the spill, concentrations obtained from these models will exceed the density of the spilled chemical. In addition to this undesirable conflict with physical behavior, the singularity does not allow initial values of concentration at the spill origin to be specified and does not reflect the initial finite volume of the space occupied by the spilled substance. Specification of the initial value of the concentration is especially useful to provide flexibility for modeling both spills of pure or undiluted substances (introduced at concentrations equal to the liquid density), as well as for releases of diluted quantities which may be assumed to occur directly into the transporting fluid or indirectly, for example, as if originally introduced into flowing drains or run-off ditches.

Several methods may be applied to develop expressions for the concentration distributions which, although based on the instantaneous point source solutions, exhibit finite behavior at the origin. In this and following subsections, alternate methods are described and characteristics of the resulting solutions are illustrated by simple examples.

(1) General Solution by Principle of Superposition

The general solution to the instantaneous point source problem which satisfies both the partial differential diffusion equation and conservation of mass is written for the one-dimensional case, with no decay, as:

$$c(x,t) = \frac{m}{\sigma_x \sqrt{2\pi}} e^{-\frac{x^2}{2\sigma_x^2}} = \frac{m}{\sqrt{2\pi}\sqrt{2 e_x t}} e^{-\frac{x^2}{4 e_x t}} \qquad (138)$$

and gives the concentration at (x,t) produced by an instantaneous source of fixed strength m located at the origin x = 0.

If the source m, in the instantaneous point source solution, is replaced by a source having a strength f(ξ) dξ and located at a spatial coordinate ξ, then the corresponding concentrations, from the point source solution, are given by:

$$c_p(x,t) = \frac{f(\xi)\ d\xi}{\sigma_x\sqrt{2\pi}}\ e^{-\frac{(x-\xi)^2}{2\ \sigma_x^2}} \qquad (139)$$

where the subscript p is used to denote point source concentrations, and the exponential term is written in terms of the distance between the location of the observation point, x, and the location of the equivalent instantaneous point source, ξ.

The method of integral solutions for distributed sources follows by taking the function f(ξ) to have some finite distribution over the spatial coordinate, and represented by a series of point sources of strength f(ξ) dξ. Since the diffusion equation is linear, the solution for the distributed source is obtained by summing the concentrations for each of these point sources so that the total concentration at the observation point x is given by the integral of the point source concentrations over the range of the function f(ξ):

$$c_d(x,t) = \int_{-\infty}^{\infty} \frac{f(\xi)}{\sigma_x\sqrt{2\pi}}\ e^{-\frac{(x-\xi)^2}{2\ \sigma_x^2}}\ d\xi \qquad (140)$$

where the subscript d is used to denote distributed source concentrations. Since for the general case the function f(ξ) may be arbitrarily defined, the limits of integration in the above are taken to extend over the entire range of the spatial coordinate. The integral is evaluated using a transformation, $\beta = \frac{(-x + \xi)}{\sigma_x\sqrt{2}}$ or $\xi = x + \beta\ \sigma_x\sqrt{2}$, to obtain:

$$c_d(x,t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} f\left(x + \beta\ \sigma_x\sqrt{2}\right) e^{-\beta^2}\, d\beta \tag{141}$$

The direct result of the transformation is to cancel the term $\sigma_x\sqrt{2}$ which appeared in the demoninator of the instantaneous point source solution and produced the singularity since $\frac{1}{\sigma_x} \rightarrow \infty$ as $t \rightarrow 0$. At time $t = 0$, the source term in the above integrand, $f(x + \beta\ \sigma_x\sqrt{2})$, reduces to $f(x)$ since $\sigma_x = \sqrt{2\ e_x t} = 0$, and the resulting initial concentration distribution becomes:

$$c_d(x,0) = \frac{f(x)}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\beta^2}\, d\beta \tag{142}$$

Using the definition of the error function, the value of the integral is obtained as $\sqrt{\pi}$, so the initial value of the concentration distribution is obtained as:

$$c_d(x,0) = f(x) \tag{143}$$

Thus, for a distributed instantaneous source, superposition yields a solution in which the initial value of the concentration distribution can be specified and, for finite values of $f(x)$, remains finite.

The above integral solution for $c_d(x,t)$ is entirely general in that it has been shown to satisfy the desired initial condition $c_d(x,0) = f(x)$

for any arbitrary spatial distribution of $f(x)$. This result is quite useful although for different types of initial distributions the evaluation of the integral expression, particularly in three dimensions for situations of practical interest, can be very compex unless simplifying assumptions are applied.

(2) Solution for Fixed Source Level

For the type of instantaneous spill conditions of interest, one appropriate distribution of initial concentration assumes a constant value, c_o, distributed symmetrically about the spill origin over an interval $-b \leq \xi \leq b$ with values of zero elsewhere. Substitution in the general integral expression gives:

$$c(x,t) = \int_{-b}^{b} \frac{c_o}{\sigma_x\sqrt{2\pi}} e^{-\frac{(x-\xi)^2}{2\sigma_x^2}} d\xi \tag{144}$$

The limits of integration are taken over the interval $-b$ to $+b$ since the contribution by values of $f(\xi)$ outside this range is zero. The subscript d on the distributed source concentration is omitted.

Using the same transformation as before, $\xi = x + \beta\,\sigma_x\sqrt{2}$, leads to:

$$c(x,t) = \frac{c_o}{\sqrt{\pi}} \int_{\frac{-b-x}{\sigma_x\sqrt{2}}}^{\frac{b-x}{\sigma_x\sqrt{2}}} e^{-\beta^2} d\beta \tag{145}$$

and evaluating the integral in terms of the error function gives the result:

$$c(x,t) = \frac{c_o}{2}\left[\operatorname{erf}\left(\frac{b+x}{\sigma_x\sqrt{2}}\right) + \operatorname{erf}\left(\frac{b-x}{\sigma_x\sqrt{2}}\right)\right] \qquad (146)$$

For values of x such that $|x| < b$ the arguments of both error function terms are positive so that the initial value for $t \to 0$ is obtained for $\sigma \to 0$ as

$$c(x,0) = \frac{c_o}{2}[1 + 1] = c_o, \qquad |x| < b \qquad (147)$$

For values of x such that $|x| > b$, the arguments of the error function terms take on opposite signs so that the initial value in this range is obtained as:

$$c(x,0) = \frac{c_o}{2}[+1 -1] = 0, \qquad |x| > b \qquad (148)$$

The total mass introduced into the system is given by $c_o \cdot 2b$; conservation of mass is satisfied then if:

$$2\,c_o b = \int_{-\infty}^{\infty} c(x,t)\,dx \qquad (149)$$

and substitution gives for the concentration integral:

$$\int_{-\infty}^{\infty} c(x,t)\,dx = \frac{c_o}{2}\int_{-\infty}^{\infty} \operatorname{erf}\left(\frac{b+x}{\sigma_x\sqrt{2}}\right)dx + \frac{c_o}{2}\int_{-\infty}^{\infty} \operatorname{erf}\left(\frac{b-x}{\sigma_x\sqrt{2}}\right)dx \qquad (150)$$

First writing the integral over a finite interval $-a < x < a$ and using the transformations $z = \frac{b + x}{\sigma_x \sqrt{2}}$ and $z = \frac{b - x}{\sigma_x \sqrt{2}}$ gives

$$\int_{-a}^{a} c(x,t)\, dx = c_o\, \sigma_x \sqrt{2} \int_{\frac{b-a}{\sigma_x\sqrt{2}}}^{\frac{b+a}{\sigma_x\sqrt{2}}} \mathrm{erf}(z)\, dz \qquad (151)$$

The integral of the error function is evaluated using:

$$\int \mathrm{erf}(z)\, dz = z\, \mathrm{erf}(z) + \frac{1}{\sqrt{\pi}}\, e^{-z^2} \qquad (152)$$

leading to the following expression for the distribution of mass over the interval $-a$ to $+a$:

$$\frac{1}{c_o\, \sigma_x \sqrt{2}} \int_{-a}^{a} c(x,t)\, dx = \left(\frac{b+a}{\sigma_x\sqrt{2}}\right) \mathrm{erf}\left(\frac{b+a}{\sigma_x\sqrt{2}}\right) + \frac{1}{\sqrt{\pi}}\, e^{-\frac{(b+a)^2}{2\,\sigma_x^2}}$$

$$- \left(\frac{b-a}{\sigma_x\sqrt{2}}\right) \mathrm{erf}\left(\frac{b-a}{\sigma_x\sqrt{2}}\right) - \frac{1}{\sqrt{\pi}}\, e^{-\frac{(b-a)^2}{2\,\sigma_x^2}} \qquad (153)$$

This expression gives the generalized result for the mass distribution as a function of time over any interval -a to +a for the distributed instantaneous source of constant initial strength. In the limit as a → ∞, the exponential terms vanish and the error function values become:

$$\operatorname{erf}\left(\frac{b + a}{\sigma_x \sqrt{2}}\right) \rightarrow 1 \tag{154}$$

$$\operatorname{erf}\left(\frac{b - a}{\sigma_x \sqrt{2}}\right) \rightarrow -1 \tag{155}$$

so that the mass integral reduces to

$$\int_{-\infty}^{\infty} c(x,t)\ dx = c_o\ \sigma_x \sqrt{2} \left[\left(\frac{b + a}{\sigma_x \sqrt{2}}\right) + \left(\frac{b - a}{\sigma_x \sqrt{2}}\right)\right] = 2\ b\ c_o \tag{156}$$

and therefore the total mass in the transporting fluid is conserved.

(3) Behavior of Particular Solution

The particular solution obtained for the illustrative case of a mass initially uniformly distributed over the interval -b to +b at a concentration of c_o was:

$$c(x,t) = \frac{c_o}{2} \left[\operatorname{erf}\left(\frac{b + x}{\sigma_x \sqrt{2}}\right) + \operatorname{erf}\left(\frac{b - x}{\sigma_x \sqrt{2}}\right)\right] \tag{157}$$

This solution was previously shown to satisfy the desired initial condition as $t \to 0$. For very large values of x, the error function terms approach opposite limits and the concentration $c(x,t)$ vanishes.

The distribution is symmetrical in x, such that $c(x,t) = c(-x,t)$ and is everywhere proportional to the initial concentration c_o (although the solution for an instantaneous point source is obtained in a form proportional to the total dispersing mass). For values of $|x| < b$, the concentration is given by the sum of two error function terms. For values of $|x| > b$, the concentration is given by the difference between two error function values, both of which approach an asymptotic limit of 1 for large argument values. Especially in this latter case, the form of the solution as written is very likely susceptible to numerical instabilities.

Figure 13 gives representative concentration distributions for the instantaneous distributed source. The illustration gives values of the ratio $\frac{c(x,t)}{c_o}$ for selected values of $\sigma_x\sqrt{2} = 1, 2,$ and 3; the half-width of the initial distribution, b, was assigned a value of 1.

As can be seen from this figure, the distribution is symmetrical in x, with a maximum value that is finite, remains at the origin, and decreases with time. For small values of time, the distribution is shorter, broader, and rises more sharply to the maximum value than the Gaussian function. For larger values of time, the distribution tends to flatten and approach the form of the Gaussian. The concentrations everywhere are proportional to the initial concentration c_o which can, for this type of model, be specified as any initial value.

(a) Time History at Origin

The concentration at the origin, $x = 0$, is given as a function of time as:

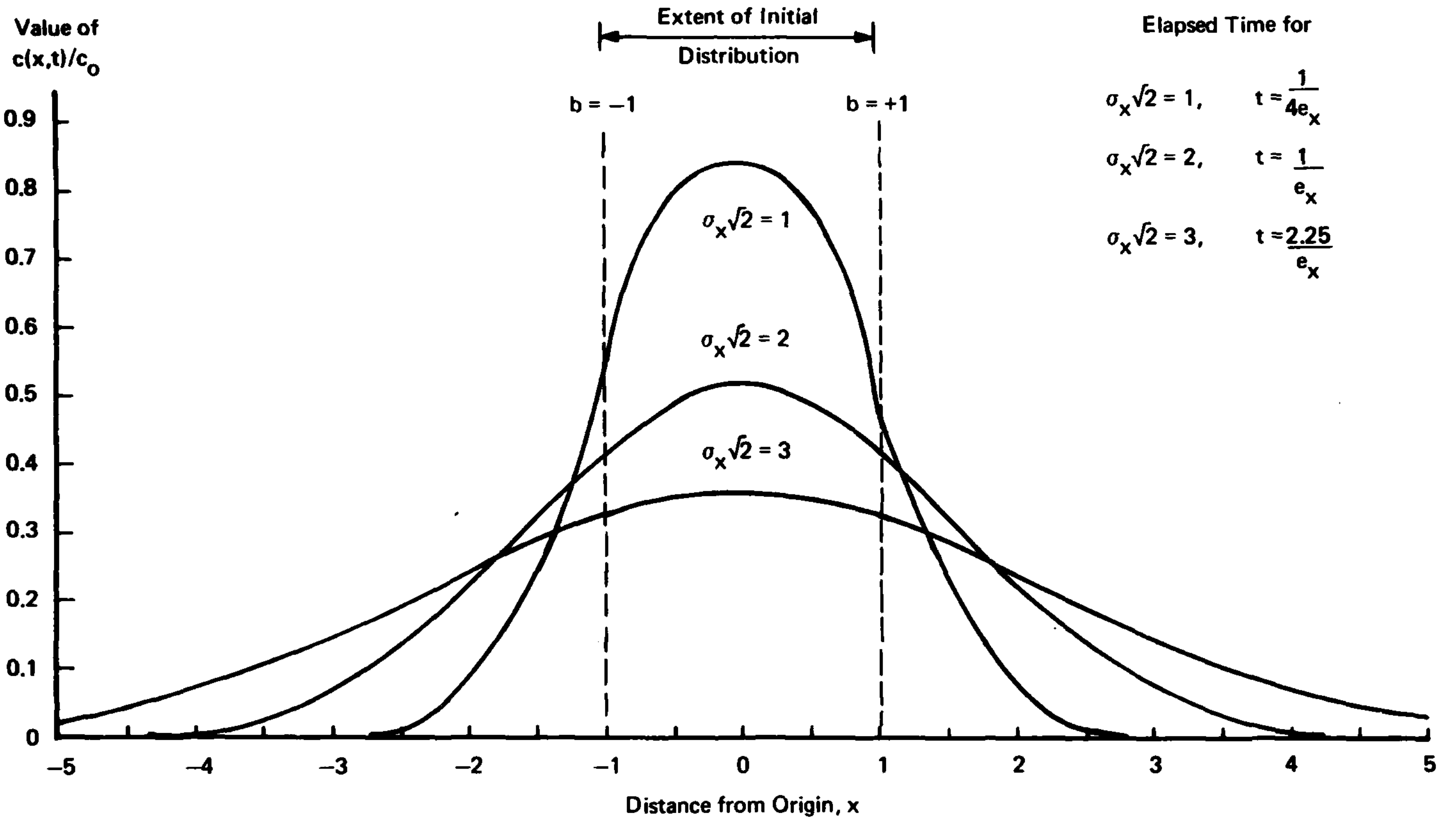


Figure 13. Distributed Instantaneous Source Concentrations

$$c(0,t) = c_o \operatorname{erf}\left(\frac{b}{\sigma_x \sqrt{2}}\right) = c_o \operatorname{erf}\left(\frac{b}{2\sqrt{e_x t}}\right) \tag{158}$$

and in the limit as t → 0 the value of the error function becomes 1.0 so that the initial value of the concentration is obtained as c_o. Since the value of the error function is approximately equal to one for values of the argument greater than 2, it can be seen that the concentration at the origin will remain approximately at the value c_o for values of:

$$\frac{b}{2\sqrt{e_x t}} > 2, \quad \text{or} \quad t < \frac{b^2}{16\ e_x} \tag{159}$$

The maximum value of the concentration distribution along the x axis occurs at the origin for all values of elapsed time greater than zero; at $t = 0$, the maximum value of c_o is distributed over $-b < x < b$.

At large values of time, the error function argument becomes small, and the approximation

$$\operatorname{erf}(\delta) = \frac{2\delta}{\sqrt{\pi}} \tag{160}$$

can be used to give:

$$c(o,t) = \frac{2\ c_o b}{2\sqrt{\pi}\sqrt{e_x t}} \tag{161}$$

Since 2 $c_o b$ gives the total mass released, it can be seen that the behavior of the distributed source approaches that of a point source for large values of time. The small argument approximation for the error function is roughly accurate up to argument values of 0.4; thus, it can be concluded that the behavior at the origin of the distributed source is approximately the same as for a point source for values of elapsed time:

$$\frac{b}{2\sqrt{e_x t}} < 0.4, \text{ or } t > \frac{b^2}{0.64\ e_x}. \qquad (162)$$

For large times, the approximate expression for the concentration at the origin can readily be inverted to obtain elapsed times at which the concentration at the origin will be reduced to any specified value. Substituting the limit of elapsed time for which the approximation is valid into the expression for concentration gives the condition that the elapsed times will be approximately accurate if the concentration c(0,t) is specified such that:

$$c(0,t) < 0.45\ c_o \qquad (163)$$

For shorter times, concentrations can be computed as a function of time using the error function expression and interpolation used to determine the elapsed times to any specific concentration at the origin.

(b) Time History at x = ± b

At an observation point $x = \pm b$, one of the error function terms in the concentration expression [Equation (157)] vanishes, leaving:

$$c(|b|,\ t) = \frac{c_o}{2}\ \mathrm{erf}\left(\frac{b}{\sqrt{e_x t}}\right) \tag{164}$$

For small values of time, the error function value is approximately 1, and the initial value of the concentration is obtained as $\frac{c_o}{2}$. This is interpreted as the mid-point between the initial values $c(b^-,0) = c_o$ and $c(b^+,0) = 0$.

For large values of time, the small argument approximation is applied for the error function, giving:

$$c(|b|,t) = \frac{2\ b\ c_o}{2\sqrt{\pi}\sqrt{e_x t}} \tag{165}$$

which is the same limit value obtained for the concentration at the origin, reflecting the nature of the spreading or flattening of the concentration distribution at large times.

(c) Time History at Point x

Since the initial condition is specified that the concentration over the interval $-b < x < b$ is equal to c_o, and the concentration is zero for all other values of x, then as the mass is dispersed, the concentrations first increase from zero for locations away from the initial zone, then decrease at some later time as the distribution tends to approach zero. Within the initial zone, $-b < x < +b$, the peak concentrations occur at $t=0$, at a value of c_o, and decrease for all elapsed times $t > 0$. For all other values of x, the time at which the concentration reaches a maximum is determined by satisfying the condition $\frac{\partial c}{\partial t} = 0$.

Using the definition of the concentration,

$$c(x,t) = \frac{c_o}{2}\left[\operatorname{erf}\left(\frac{b+x}{2\sqrt{e_x t}}\right) + \operatorname{erf}\left(\frac{b-x}{2\sqrt{e_x t}}\right)\right] \tag{166}$$

and the derivative of the error function:

$$\frac{\partial}{\partial t}\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} e^{-z^2} \frac{\partial z}{\partial t} \tag{167}$$

leads to

$$\frac{\partial c(x,t)}{\partial t} = -\frac{c_o}{4\sqrt{\pi}\sqrt{e_x}\, t^{3/2}}\left[(b+x)\, e^{-\frac{(b+x)^2}{4 e_x t}} + (b-x)\, e^{-\frac{(b-x)^2}{4 e_x t}}\right] \tag{168}$$

Expanding the exponential terms, factoring out common terms, and setting $\frac{\partial c}{\partial t} = 0$ give a condition for a maximum concentration as:

$$(x+b)\, e^{-\frac{bx}{2 e_x t_{max}}} - (x-b)\, e^{+\frac{bx}{2 e_x t_{max}}} = 0 \tag{169}$$

which gives

$$e^{-\frac{bx}{e_x t_{max}}} = \frac{x-b}{x+b}, \qquad x > b \tag{170}$$

According to this equation, the value of the exponential function is close to 1 if x is much larger than b (or for large values of time), and a first order approximation gives

$$1 - \frac{bx}{e_x t_{max}} = \frac{x - b}{x + b} \tag{171}$$

and solving for t_{max} yields

$$t_{max} = \frac{x\ (x + b)}{2\ e_x} \tag{172}$$

which reduces to the same expression obtained for the instantaneous point source since x >> b. The similar behavior at long distances between the point and distributed sources is again observed.

At values of x closer to b, solving directly for t_{max} gives

$$t_{max} = \frac{bx/e_x}{\ln\ (x + b) - \ln\ (x - b)} \tag{173}$$

and it can be seen that $t_{max} \to 0$ as $x \to b$.

The envelope of maximum concentrations can be obtained by selecting values of x, computing the corresponding times to the maximum concentration, and then substituting the values of the (x,t) pairs in the error function expression to compute the value of the concentration.

The concentration time history at any point x can also be simply obtained by computing the concentration as a function of the value of x and a range of values of time. Since the maximum concentration occurs at a time, t_{max}, the time interval of interest for the concentration history is given by intervals both preceding the following t_{max}. Approximate limits for the range of elapsed times to be considered can be taken from the time history of the concentration at the origin, selecting times corresponding to concentrations both greater and less than the maximum value which occurs at the location x. The lower limit of time may also be taken as 0 or some intermediate value between 0 and t_{max}.

(d) Extent of Hazard

For the instantaneous point source, it was possible to obtain an analytical expression for distance as a function of time and a fixed concentration, allowing for the computation of the distance x (as a function of time) over which concentrations would exceed a specified hazard level.

Since an equivalent analytical result is not readily obtained for the distributed source, the alternative is to use the concentration equation (166) to obtain, for various elapsed times, the distribution over x of maximum concentrations. For each value of elapsed time, interpolation can then be applied to bracket the specified concentration level and determine the range over which it exists. Since the maximum concentration over all values of x occurs at the origin, the maximum time for which the hazard exists anywhere in the aquatic environment is given by the time over which the concentration at the origin exceeds the specified level.

(e) Solution for Non-Conservative Chemical

The method of obtaining a solution for the distributed source proceeds by integrating the concentrations from a series of point sources over the spatial coordinate range of the distributed source function. Since for a point source the decay is introduced through an exponential factor, e^{-kt}, which does not affect the integration, the result for an initially constant distribution over $-b < x < b$ of a decaying chemical is simply:

$$c(x,t) = \frac{c_o}{2} e^{-kt} \left[\mathrm{erf}\left(\frac{b + x}{\sigma_x \sqrt{2}}\right) + \mathrm{erf}\left(\frac{b - x}{\sigma_x \sqrt{2}}\right) \right] \tag{174}$$

The time history at the origin becomes:

$$c(0,t) = c_o \, e^{-kt} \, \mathrm{erf}\left(\frac{b}{\sigma_x \sqrt{2}}\right) \tag{175}$$

and since the error function remains approximately constant at a value of 1.0 for $t < \frac{b^2}{16\, e_x}$, the concentration at the origin now experiences immediate reduction according to the behavior of e^{-kt}.

Since the concentration at any location x is obtained as the product of the exponential e^{-kt} and the *concentration distribution for* k = 0, the condition for the maximum value of the concentration at x is given by:

$$\frac{\partial}{\partial t} c_{k>0}(x,t) = \frac{\partial}{\partial t} c_{k=0}(x,t) \; e^{-kt} \tag{176}$$

and the derivative of $c_{k>0}(x,t)$ with respect to time is zero at:

$$\frac{\partial \, c_{k=0}(x,t)}{\partial t} - k \, c_{k=0}(x,t) = 0 \tag{177}$$

and the maximum concentration at x has a lower value and occurs at an earlier time than if k = 0, as expected.

(4) Observations

If the volume or length for the one-dimensional example, within which an instantaneous spill is initially contained can be described, then superposition of concentration distributions from a series of instantaneous point source releases yields an integral solution for the concentrations from a distributed source. These concentrations remain finite in the vicinity of the spill, and thus initial values for the concentration at the spill origin may be specified to be consistent with physical behavior.

As the chemical mass is dispersed in the transporting fluid, turbulent mixing will dissipate the effects of the initial mass distribution so that at sufficiently long times the concentrations should approach a Gaussian distribution, becoming independent of the initial mass configuration. The results obtained for the example one-dimensional case exhibited this behavior. Also, the distributed source modeled by this integral approach satisfies conservation of mass and presents a reasonably realistic concentration distribution within the overall assumptions of the model.

Except for highly idealistic cases, however, the integrals involved, especially in two or three dimensions,are extremely difficult to carry out, and numerical methods will usually be required. This is a significant disadvantage considering that the numerical integrations must be performed repetitively for different coordinates of the observation point and elapsed times.

A second disadvantage is the apparent uncertainty of an ability to reasonably assume and describe the geometry of the initial mass distribution, particularly considering the influence of environmental conditions and the nature of the discharge (accident, explosion, etc.) for the situations of interest in this context, although for other types of discharges the discharge distribution can be quite precisely known. In turn, near the spill location the concentrations obtained from the distributed source solution are significantly dependent on the assumed geometry and thus subject to the same uncertainties. Two alternate approaches for adapting Gaussian models to estimate finite concentration behavior in the locale of a discharge, with less dependence on the geometry of the initial mass distribution, are described in the two following subsections.

c. Virtual Source

Since the instantaneous point source produces a concentration distribution that does not provide for finite initial concentrations at the spill location nor an initial finite distribution in spatial coordinates of the dispersing mass, the method of virtual sources is sometimes utilized. Simply, the instantaneous point source solution continues to be utilized, but translations in time and spatial coordinates are employed to delay the point source solution until some set of desired characteristics have been reached; this intermediate point in the Gaussian distribution is then taken to be the initial condition for the spill being modeled. The transformation is taken in time or, in the case of a moving river, the river velocity, and the time delay which are used to obtain an equivalent upstream offset for the location of the virtual source.

Since the dispersion coefficients, σ_x in one-dimension or σ_x, σ_y and σ_z in three dimensions, convey measures of the extent of spreading of the dispersing mass, the modeling accuracy obtainable will depend on the degree to which the volume described by σ_x, σ_y, and σ_z after the time of delay is appropriate for the type of release and description of the initial volume. If the dispersion coefficients are equal, constant concentration values will lie on a spherical surface; the dispersing mass is visualized as being contained within a spherical volume which increases in size with time. If the dispersion coefficients are unequal, the volume shape is given as a three-dimensional ellipsoid. Further, if there are significant differences in the values of the dispersion coefficients in the axis directions, then the shape of the ellipsoid may become considerably distorted. The fastest growth occurs in the direction in which the dispersion coefficient is greatest, and if sufficiently distorted, the representation may be more appropriate for line or area sources but not volume sources. In any case, the shape of the volume within which any desired fraction of the total dispersing mass is contained after any elapsed time is directly dependent on the values of the dispersion coefficients.

(1) Determination of Delay Time

For an instantaneous point source, the Gaussian distribution gives concentrations at the center of the dispersing mass in the form for one-dimension:

$$c(0,t) = \frac{m}{2\sqrt{\pi}\sqrt{e_x t}} \tag{178}$$

in which $c(0,t) \to \infty$ as $t \to 0$. To obtain a solution in which the initial value of the concentration is desired to be a value c_o, the elapsed time at which the Gaussian distribution reaches this value:

$$t_d = \frac{m^2}{4\,\pi\,e_x\,c_o^2} \tag{179}$$

defines the delay time for the virtual source. That is, if t is used to measure elapsed time from the start of the modeled spill, then the appropriate elapsed time from the start of the virtual spill is $t + t_d$. Then the form of the Gaussian distribution is used with this substitution, i.e., $c(x,t+t_d)$ is used to obtain the concentration at (x,t). Note that the resulting distribution is still a point source solution; however, the location of the point has been translated to $x = 0$, $t = -t_d$, out of the time frame of interest.

The nature of the distribution obtained from a virtual source assumption is described by the characteristics of the Gaussian distribution at an elapsed time equal to t_d. Since the effects of the initial distribution of spilled mass are diminished over time by turbulent mixing, and concentrations should approach a Gaussian distribution as time increases, the virtual source gives a good method of obtaining finite initial conditions since it is by definition Gaussian.

(2) Behavior of Solution

For the one-dimensional case, the concentration distribution for a virtual source is given by:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x(t+t_d)}}\ e^{-\frac{x^2}{4\ e_x(t+t_d)}} \qquad (180)$$

where t gives the elapsed time from the start of spill being modeled and t_d gives the delay time from the start of the virtual spill to $t = 0$.

(a) Mass Distribution

Since the distribution of mass is determined by integration over the spatial coordinate, the expression is obtained from the point source solution by substituting $t + t_d$:

$$m(x,t) = m \cdot \text{erf}\left(\frac{x}{2\sqrt{e_x}\sqrt{t+t_d}}\right) \tag{181}$$

At time $t = 0$, the mass has an initial distribution determined by $\sigma_x = \sqrt{2\ e_x\ t_d}$ such that 68 percent of the mass is contained in an interval of width $2\sigma_x$ and 95 percent of the mass is contained in an interval of width $4\sigma_x$.

The maximum concentration is c_o at $x = 0$. Expressing t_d in terms of c_o gives the following for the initial average concentration:

$$\text{Initial average over interval of width } 2\sigma_x = \frac{0.68m}{2\sqrt{2\ e_x\ t_d}} = 0.85\ c_o \tag{182}$$

$$\text{Initial average over interval of width } 4\sigma_x = \frac{0.95m}{4\sqrt{2\ e_x\ t_d}} = 0.60\ c_o \tag{183}$$

(b) Time History at Origin

The concentration at the origin is given as a function of time by:

$$c(0,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x(t+t_d)}} \tag{184}$$

Since t_d can be written in terms of the initial concentration, c_o, expressing the elapsed time t as a multiple of t_d, $t = s \cdot t_d$ where $s \geq 0$, leads to the simplification:

$$c(0,t) = \frac{c_o}{\sqrt{s+1}}, \qquad s \geq 0 \tag{185}$$

As t varies from 0 to ∞, s has the same range and the concentration varies from c_o to 0.

Inverting the equation gives:

$$s = \left[\frac{c_o}{c(0,t)}\right]^2 - 1 \tag{186}$$

which, since $t = s \cdot t_d$, expresses the time at which the concentration at the origin reaches a specified value of c(0,t). As the concentration at the origin is reduced, the time s at which any particular concentration is reached approaches the same value as for an instantaneous point source release. The maximum duration during which concentrations will exceed a particular hazard level, for any value of x, is obtained by computing the value of s corresponding to the desired concentration.

(c) Time History at Point x

For the virtual source solution, obtained as a time-delayed point source solution, the initial concentrations along the spatial coordinate are non-zero, being given by:

$$c(x,0) = \frac{m}{\sqrt{2\pi}\sqrt{2\, e_x\, t_d}}\, e^{-\frac{x^2}{4\, e_x\, t_d}} = c_o\, e^{-\frac{x^2}{4\, e_x\, t_d}} \qquad (187)$$

The initial concentrations become small as x increases in value above $\sqrt{2\, e_x\, t_d}$.

For elapsed times greater than zero, the maximum concentration, at a fixed value of x, is determined from:

$$\frac{\partial c}{\partial t} = \frac{c(x,t)}{(t+t_d)} \left[\frac{x^2}{4\, e_x\, (t+t_d)} - \frac{1}{2} \right] = 0 \qquad (188)$$

Since the virtual source gives a delayed Gaussian curve, for a region near the location of the spill, the maximum concentration would have occurred (for the Gaussian during the delay period) at a time $t < 0$, and it can be seen from the above that for small values of x the derivative is negative. At time $t = 0$, the derivative is zero for $x = \sqrt{2\, e_x\, t_d}$, and therefore for values of $x < \sqrt{2\, e_x\, t_d}$, the maximum concentration occurs at time $t = 0$ and is given by

$$c(x,t_{max}) = c_o\, e^{-\frac{x^2}{4\, e_x\, t_d}}, \qquad x < \sqrt{2\, e_x\, t_d},\ t_{max} = 0 \qquad (189)$$

For locations $x > \sqrt{2\, e_x\, t_d}$, the maximum concentration occurs at a time t_{max} given by

$$t_{max} = \frac{x^2}{2\, e_x} - t_d \qquad (190)$$

The concentration at this time and location is:

$$c(x,t_{max}) = \frac{e^{-1/2}}{\sqrt{2\pi}} \cdot \frac{m}{x} = 0.24197 \frac{m}{x}, \qquad x > \sqrt{2\ e_x\ t_d} \tag{191}$$

which is the same value as obtained for the instantaneous point source. Thus, at distances greater than $\sqrt{2\ e_x\ t_d}$, the maximum concentration level reached from a virtual source is the same as if an instantaneous point source were assumed but it occurs at a time t_d earlier.

These equations give the coordinates on the envelope of maximum concentration as a function of distance as:

$$\text{for } 0 < x < \sqrt{2\ e_x\ t_d}, \qquad t_{max} = 0$$

$$c(x,t_{max}) = c_o\ e^{-\frac{x^2}{4\ e_x\ t_d}} \tag{192}$$

$$\text{for } x > \sqrt{2\ e_x\ t_d}, \qquad t_{max} = \frac{x^2}{2\ e_x} - t_d$$

$$c(x,t_{max}) = \frac{m \cdot e^{-1/2}}{x\sqrt{2\pi}} \tag{193}$$

and are plotted in Figure 14 for an example using $e_x\ t_d = 0.25$, together with an equivalent point source envelope for comparison. It can be seen that the effect of the virtual source is to translate the elapsed time by $e_x\ t_d$, and for distances close to the spill ($x < \sqrt{2\ e_x\ t_d}$) the maximum

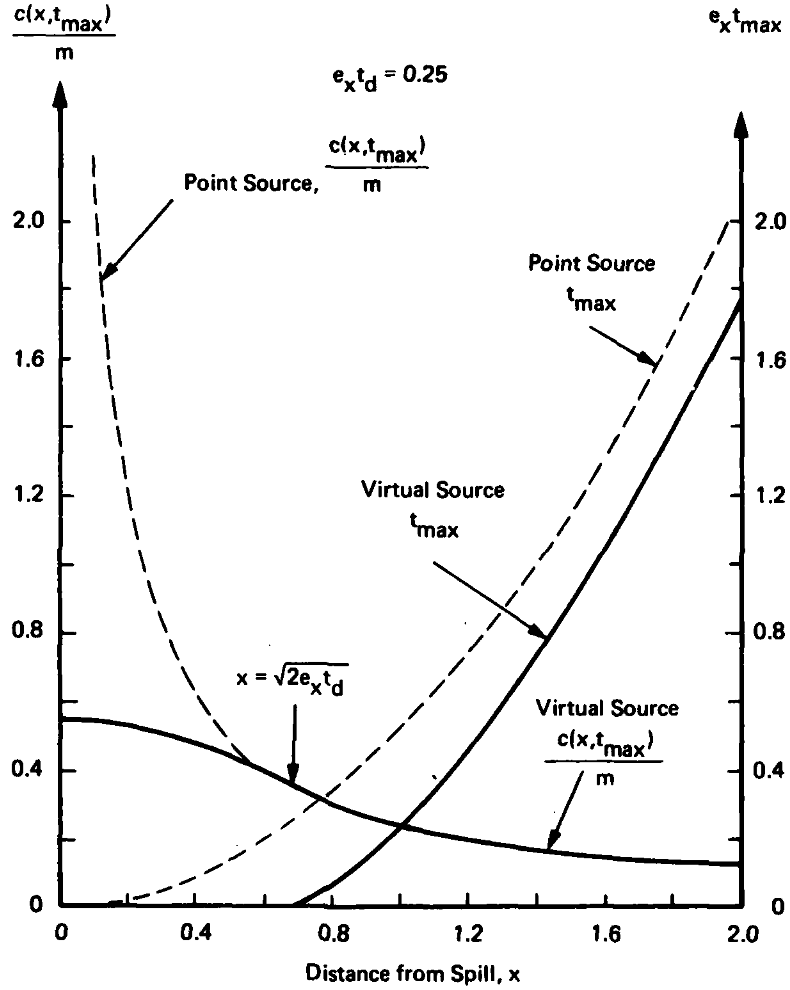


Figure 14. Concentration Envelope Versus Distance (Virtual Source)

concentration behaves as a decaying exponential distribution, becoming equal to the point source values at $x = \sqrt{2\, e_x\, t_d}$.

To compare the virtual source and point source envelopes, Figure 14 gives the concentration as the ratio $\frac{c(x, t_{max})}{m}$; the initial concentration, c_o, is expressed in terms of m by:

$$c_o = \frac{m}{\sqrt{\pi}\sqrt{4\, e_x\, t_d}} \tag{194}$$

The concentration at the point on the envelope at which the virtual source and the point source curves meet is obtained as:

$$c(x, t_{max}) = \frac{m\, e^{-1/2}}{\sqrt{\pi}\sqrt{4\, e_x\, t_d}}, \qquad x = \sqrt{2\, e_x\, t_d} \tag{195}$$

The equations for the concentration envelope can readily be inverted to obtain maximum distances in terms of specified concentrations:

For $c_o > c(x, t_{max}) > c_o\, e^{-1/2}$, the specified maximum concentration $c(x, t_{max})$ occurs at time $t_{max} = 0$, and at a distance given by

$$x = \sqrt{4\, e_x\, t_d}\left[\ln\left(\frac{c_o}{c(x, t_{max})}\right)\right]^{1/2} \tag{196}$$

For $c(x,t_{max}) < c_o\, e^{-1/2}$, the specified maximum concentration $c(x,t_{max})$ occurs at a distance of

$$x = \frac{c_o}{c(x,t_{max})} \sqrt{2\, e_x\, t_d}\; e^{-1/2} \tag{197}$$

and the time at which this occurs is given by $t_{max} = \frac{x^2}{2\, e_x} - t_d$.

Limits on expected concentrations can be used to estimate the times and distances over which concentrations of interest will exist and thus determine bounds on time and distance scales.

Since the concentration variation, at any location x, with time is expressed using a Gaussian distribution with time $\tau = t + t_d$, the concentrations occurring at point x will behave as shown in Figure 10 for the point source solution, with a translation of the time axis such that $t = \tau - t_d$. The concentration values indicated in Figure 10 remain at the same level, but the entire curve is translated in time by an amount t_d so that the concentration at $t = 0$ is greater than zero. It can be seen that, for values of x close to the spill site, the translation will move the time for which the maximum point source concentration occurs to a value of $t < 0$.

(d) Extent of Hazard

By inverting the equation for concentration, the distance at which a specified concentration occurs can be obtained as a function of concentration and time:

$$x^2 = 4\ e_x(t + t_d) \cdot \ln \left[\frac{c_o/c(x,t)}{\sqrt{1 + t/t_d}} \right],\ c(x,t) \leq c_o \qquad (198)$$

These distances are defined for times such that the argument of the logarithm is greater than or equal to 1, which gives a constraint on time for any given concentration as:

$$t < t_d \left[\frac{c_o^2}{c^2(x,t)} - 1 \right] \qquad (199)$$

At the limit of elapsed time, the specified concentration occurs only at the spill location, and the distance x is equal to zero.

(e) Solution for Non-Conservative Chemical

Where decay or degradation of the chemical in the environment is assumed to occur, a decay term is applied to the concentration distribution for the virtual source, giving:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\ \sqrt{2\ e_x(t+t_d)}}\ e^{-\frac{x^2}{4\ e_x(t + t_d)}}\ e^{-kt} \qquad (200)$$

and the mass distribution over an interval of 2x, centered at the spill location, becomes:

$$m(x,t) = m\ e^{-kt}\ \mathrm{erf} \left(\frac{x}{2\sqrt{e_x}\sqrt{t + t_d}} \right) \qquad (201)$$

In this formulation the mass m is introduced instantaneously at time $t = 0$, and has an initial distribution determined from the Gaussian at time $t = t_d$ such that the concentration at the spill location is c_o. A larger equivalent mass is associated with the start of the virtual spill so that the decay over the interval t_d gives the total mass m at $t = 0$.

The time history of the concentration at the origin is given by

$$c(0,t) = \frac{m\ e^{-kt}}{\sqrt{2\pi}\sqrt{2\ e_x(t + t_d)}} \tag{202}$$

and at $t = 0$ the initial value is

$$c(0,0) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x\ t_d}} = c_o \tag{203}$$

For the maximum concentration at any location x, the derivative of the concentration with respect to time gives:

$$\frac{\partial c}{\partial t} = \left[\frac{x^2}{4\ e_x(t + t_d)^2} - \frac{1}{2(t + t_d)} - k\right] \cdot c(x,t) \tag{204}$$

At time $t = 0$, the derivative is zero for

$$x^2 = 2\ e_x\ t_d + 4\ k\ e_x\ t_d^2 \tag{205}$$

and the width of the interval over which the maximum concentrations occur at $t = 0$ is extended by the presence of the decay term. For larger values of x, the time the maximum concentration occurs, t_{max}, can be obtained from:

$$\frac{1}{t_{max} + t_d} = \frac{e_x}{x^2} + \frac{e_x}{x^2}\sqrt{1 + \frac{4\ x^2\ k}{e_x}} \tag{206}$$

and the corresponding value of concentration is obtained by substituting the values of x and $t = t_{max}$ in the equation for $c(x,t)$.

The distance at which a specified concentration exists as a function of time can be obtained from:

$$x^2 = 4\ e_x(t + t_d) \left\{ \ln \left[\frac{m}{2\ c(x,t)\sqrt{\pi\ e_x(t + t_d)}} \right] - kt \right\} \tag{207}$$

For values of $t > 0$, this expression is zero for

$$\sqrt{t + t_d}\ e^{kt} = \frac{m}{2\ c(x,t)\sqrt{\pi\ e_x}} \tag{208}$$

and this gives the condition determining whether the concentration has the value $c(x,t)$ at a location $x > 0$ at the value of time specified.

d. Modified Source

The concentration distribution from an instantaneous point source is given as:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x t}}\ e^{-\frac{x^2}{4\ e_x t}} \tag{209}$$

where the initial concentrations are zero for $|x| > 0$, but infinite at $x = 0$. Conversely, the virtual source distribution given by

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x(t + t_d)}}\ e^{-\frac{x^2}{4\ e_x(t + t_d)}} \tag{210}$$

gives an initial distribution of non-zero concentrations for $|x| > 0$, and a finite initial value of c_o at $x = 0$.

(1) Form of Solution

Characteristics of both forms of solution can be combined by using a modified form of the distribution written as:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\ \sqrt{2\ e_x(t + t_d)}}\ e^{-\frac{x^2}{4\ e_x t}} \tag{211}$$

For values of $|x| > 0$,this gives the point source behavior that the initial concentrations are zero. However, at the origin, $x = 0$, the expression also gives a finite initial value of the concentration:

$$c(0,0) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x\ t_d}} \tag{212}$$

which applied to the virtual source.

It can be seen that, in this modified solution, the concentration can be visualized as resulting from the distribution of the mass m over an interval of length proportional to $\sqrt{2\ e_x(t + t_d)}$. The point source produces infinite concentrations at the spill location as a result of this length vanishing as $t \to 0$. However, in the modified solution the length has a value, $\sqrt{2\ e_x\ t_d}$, greater than zero at $t = 0$, and the concentration at the origin remains finite as $t \to 0$.

Since initially the concentrations at all other values of x are zero, it can be inferred that this form of the solution does not satisfy conservation of mass. This is verified by integrating over the spatial coordinate x to give:

$$m(x,t) = \frac{\sqrt{t}}{\sqrt{t + t_d}}\ \mathrm{erf}\left(\frac{x}{\sqrt{4\ e_x t}}\right) \tag{213}$$

where m(x,t) gives the total mass in an interval about the origin $-x$ to $+x$. The total mass distributed along the line is obtained for $x \to \infty$ as a function of time:

$$m(t) = \frac{m}{\sqrt{1 + \frac{1}{s}}}, \qquad t = s\ t_d \tag{214}$$

so that conservation of mass is not satisfied, although as s becomes large, $m(t) \to m$. The time parameter, s, is tabulated below for a range of values of the ratio m(t)/m:

m(t)/m	s
0.1	0.010
0.2	0.042
0.3	0.099
0.4	0.190
0.5	0.333
0.6	0.562
0.7	0.961
0.8	1.778
0.9	4.263
0.95	9.256
0.99	49.250

For values of $s < 1$ or $t < t_d$, the total amount of mass rises rapidly as s varies from 0 to 1, that is, from 0 to $m(t) = \sqrt{2}\, m/2$ at $s = 1$. Further increase for larger values of s occurs much more slowly, so that m(t) does not reach 95 percent of m until $t = 9.256\ t_d$. Conservation of mass states that the total amount of mass discharged remains constant in the environment in the absence of any sources or sinks; therefore, the solution behaves as if a time-varying discharge takes place.

The concentration distributions for the point source and the modified source can be compared by writing these equations in terms of the initial concentration of the modified source to obtain:

$$\text{for the point source, } c(x,t) = \frac{c_o\sqrt{t_d}}{\sqrt{t}}\, e^{-\frac{x^2}{4\, e_x t}} \tag{215}$$

and,

$$\text{for the modified source, } c(x,t) = \frac{c_o\sqrt{t_d}}{\sqrt{t + t_d}}\, e^{-\frac{x^2}{4\, e_x t}} \tag{216}$$

Letting $t = s\ t_d$ and $x = r\ \sigma_x$ where $\sigma_x = \sqrt{2\ e_x t}$ and s and r are non-dimensional parameters greater than zero gives the concentrations in the form:

$$\text{Point source, } \frac{c_o}{\sqrt{s}}\, e^{-\frac{r^2}{2}} \tag{217}$$

$$\text{Modified source, } \frac{c_o}{\sqrt{s + 1}}\, e^{-\frac{r^2}{2}} \tag{218}$$

These expressions are plotted in Figure 15 for values of s = 0.5, 1.0, 1.5, and 2.0, and for r ranging from 0 to 3.0. Both solutions exhibit similar behavior, and the point source solution gives concentrations that are everywhere greater than those from the modified source. In Figure 15(a), where s = 0.5, it can be seen that the point source gives a concentration estimate about 41 percent greater than c_o at the origin, and concentrations greater than c_o over a distance r of approximately 0.8.

Since the form of the concentration expressions contains the same dependence on distance, x, the ratio of the concentrations is constant for all values of x. The magnitude of the ratio depends only on elapsed time t:

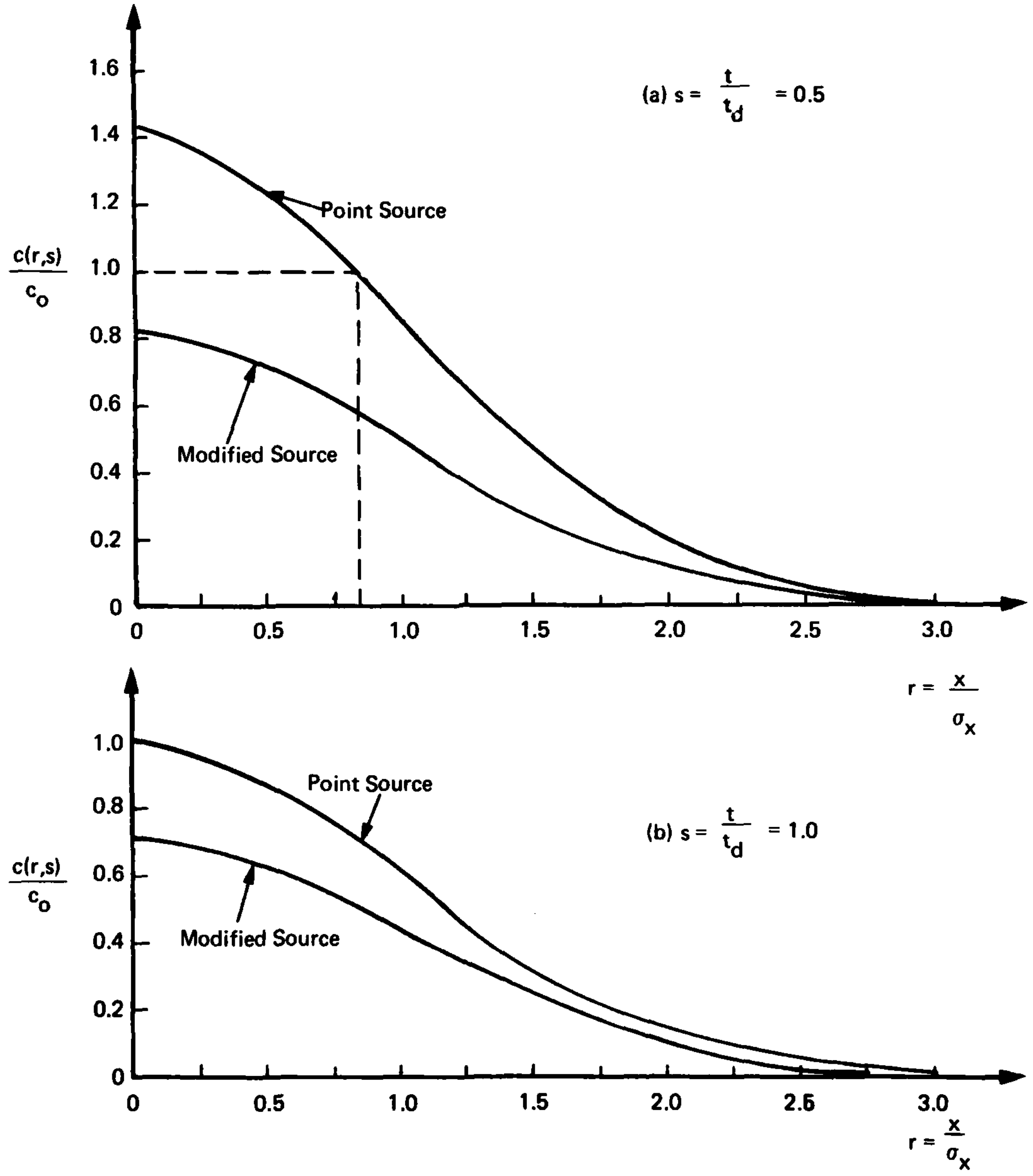


Figure 15. Ratio of Concentration to Initial Value

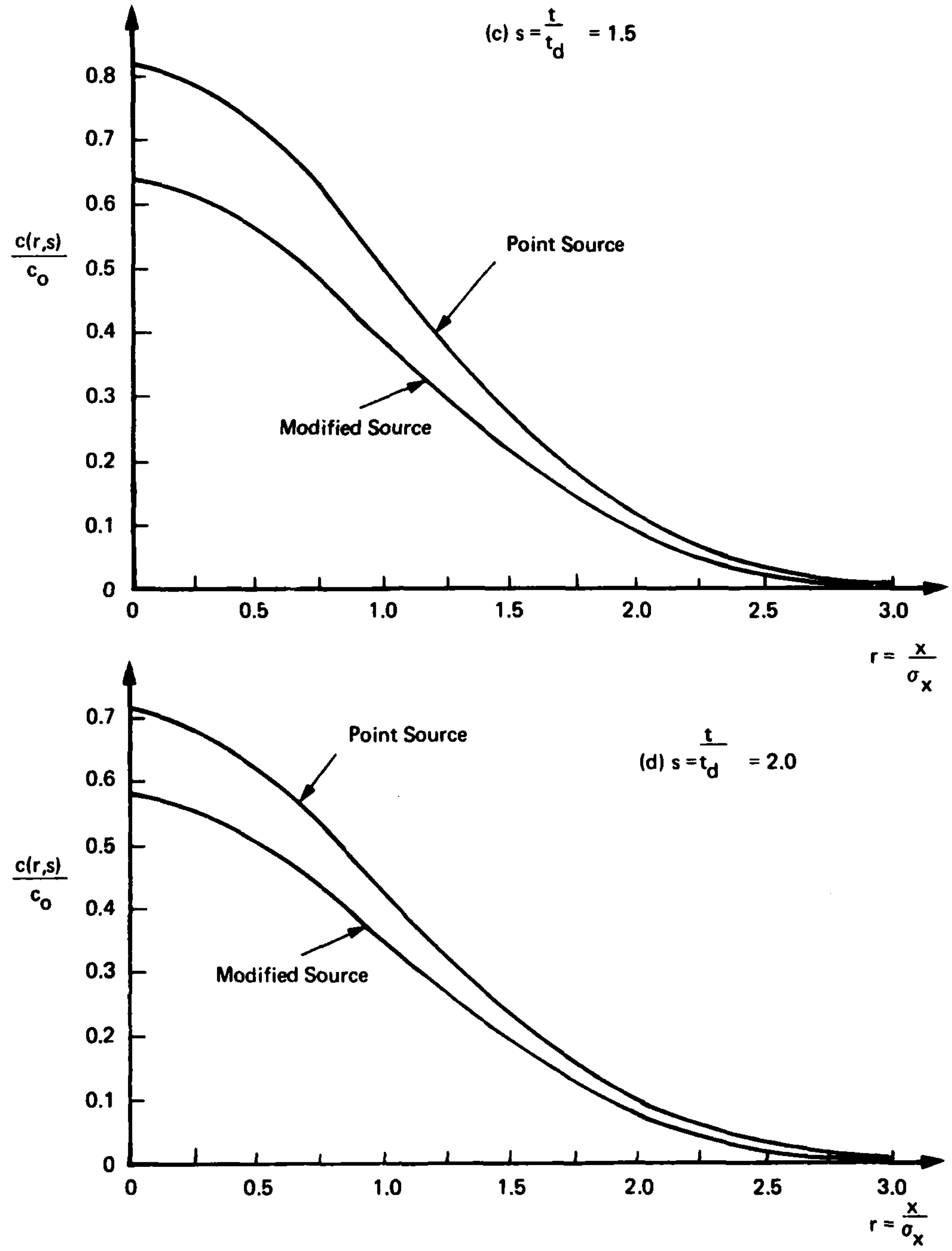


Figure 15. Ratio of Concentration to Initial Value (Concluded)

$$\frac{c(x, s\ t_d) \text{ for modified source}}{c(x, s\ t_d) \text{ for point source}} = \frac{\sqrt{s}\sqrt{s+1}}{s+1} \tag{219}$$

Values of this ratio, plotted in Figure 16, show a very rapid increase from 0 at $t = 0$, where the point source concentration is infinite, to a value of 0.707 at $s = 1$, then gradually increasing, approaching a limit value of 1 as s becomes large.

(2) Determination of Delay Time

The modified solution gives an expression for the time history at the origin which can be inverted to solve for the delay time t_d in terms of the concentration at $x = 0$, $t = 0$:

$$t_d = \frac{m^2}{4 \pi e_x c(0,0)} \tag{220}$$

and the value of t_d can be computed to obtain any desired initial concentration condition at the origin.

If the value used for $c(0,0)$ is very large, t_d will be small and the solution obtained from the modified source will give a closer approximation to a point source at smaller values of elapsed time. From Figure 16, at a value of $s = \frac{t}{t_d} = 4.5$, the ratio of concentrations is approximately 0.904, and reducing t_d will reduce the value of t at which this ratio is reached.

(3) Behavior of Solution

A preceding subsection described the distribution of mass associated with the modified source and showed that conservation of mass is not satisfied

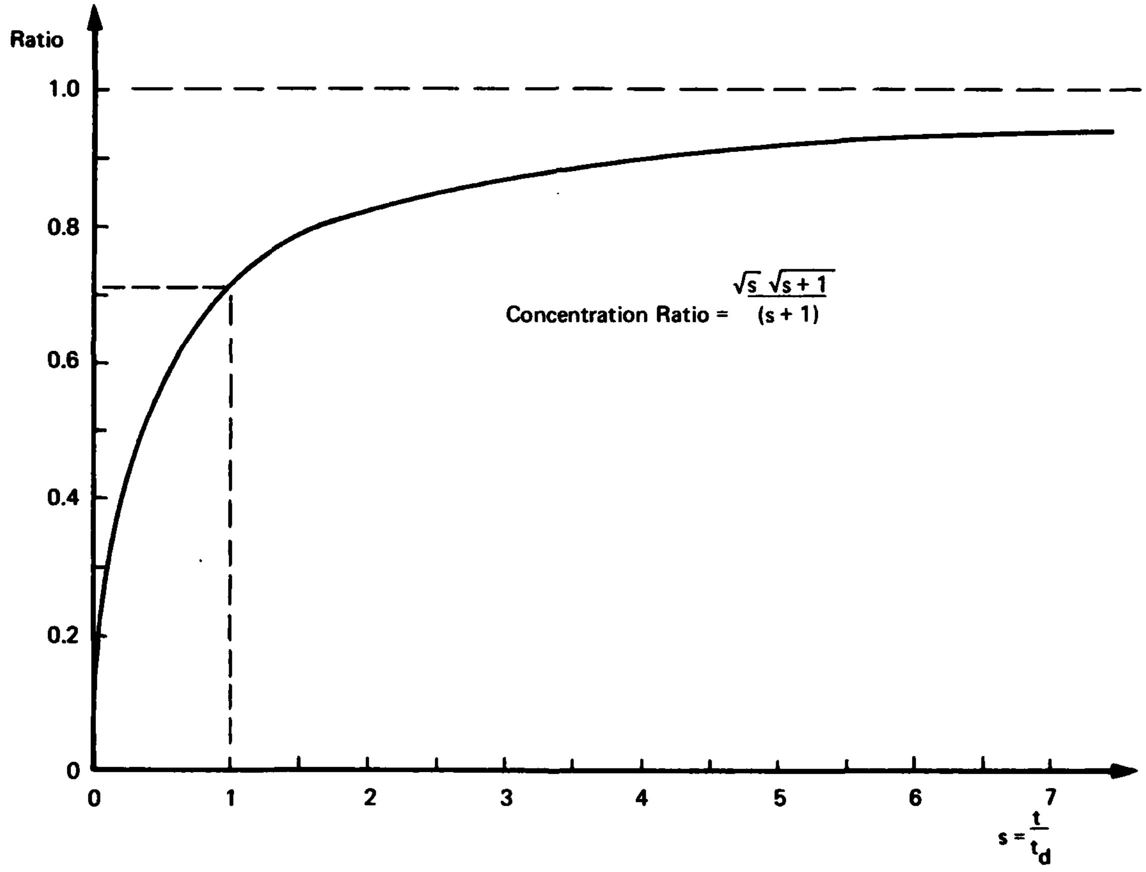


Figure 16. Concentration Ratio

for this solution, although the total quantity of dispersing mass approaches a constant at large times. Other characteristics of this form of the solution are described in the following paragraphs.

(a) Time History at Origin (x = 0)

The concentration at the origin is given by

$$c(0,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x(t + t_d)}} \tag{221}$$

and this value is the maximum concentration over all values of x at this value of time. The constant t_d is determined by the desired initial value of concentration at t = 0, c_o, and using this value, the equation for concentration can be used to solve for the elapsed time at which any given value of concentration is reached:

$$\frac{t}{t_d} = \left[\frac{c_o^2}{c^2(0,t)} - 1\right] \tag{222}$$

Figure 17 shows the ratio $\frac{c(0,t)}{c_o}$ as a function of the ratio $\frac{t}{t_d}$.

(b) Time History at Point x

Since the concentrations given by the modified solution are initially zero for all values of $|x| > 0$ and are zero for very large values of time, at any point x, at some time after the spill occurs, the concentration observed increases to a maximum value and then decreases as further dispersion takes place. The derivative with respect to time is:

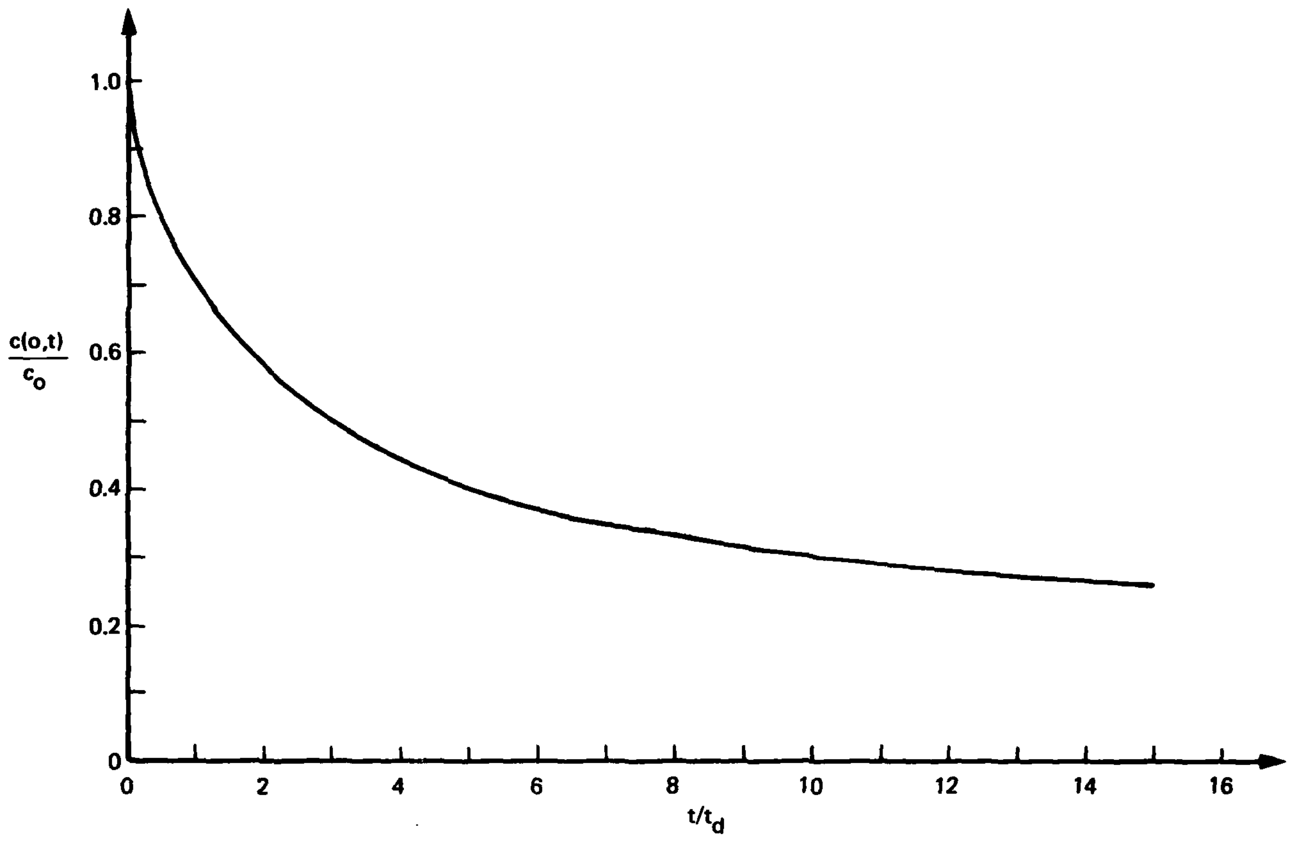


Figure 17. Time History at Origin (Modified Source)

$$\frac{\partial c}{\partial t} = \left[\frac{x^2}{4\ e_x t^2} - \frac{1}{2(t + t_d)} \right] c(x,t) \tag{223}$$

and this is zero at t_{max} where:

$$t_{max} = \frac{x^2}{4\ e_x} + \frac{x^2}{4\ e_x} \sqrt{x^2 + 8\ e_x\ t_d} \tag{224}$$

This equation for the time at which the maximum concentration occurs reduces to the same expression as for a point source when $t_d = 0$. For the modified solution, the maximum concentration at any location x occurs at a later time than for a point source. The magnitude of this concentration is obtained by substituting the values of x, t_{max} in the equation for c(x,t).

The envelope of maximum concentrations is determined by the values of t_{max} and $c(x,t_{max})$ as a function of x. Figure 18 gives a sample envelope for $e_x\ t_d = 0.25$, together with an equivalent point source envelope for comparison. The time at which the maximum occurs for the modified source is delayed, and the maximum value, initially less than that for a point source, approaches the point source value as the distance increases.

(c) Extent of Hazard

Using the concentration equation to solve for distance in terms of concentration and elapsed time leads to:

$$x^2 = 4\ e_x t\ \ln \left[\frac{c_o/c(x,t)}{\sqrt{1 + t/t_d}} \right], \qquad c(x,t) \leq c_o \tag{225}$$

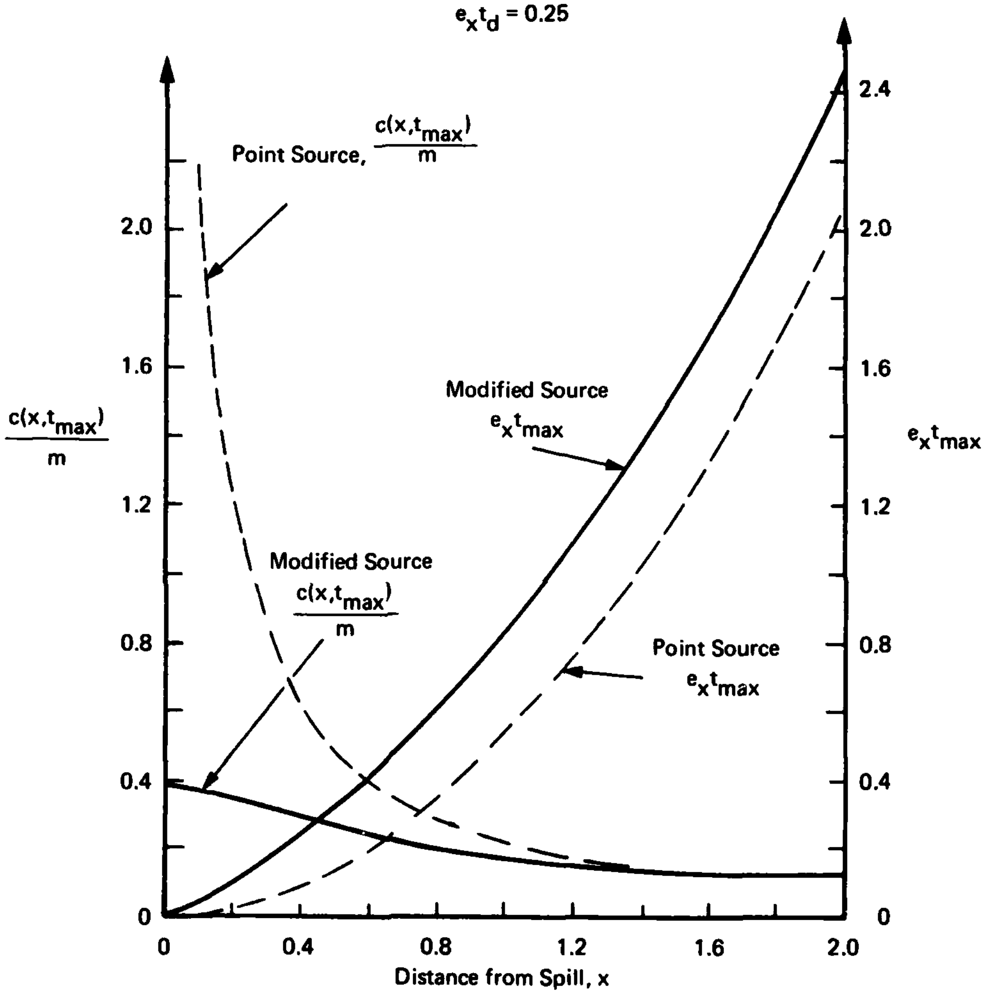


Figure 18. Concentration Envelope Versus Distance (Modified Source)

This expression is almost identical to that for a virtual source, and the same constraint applies, that is,

$$t < t_d \left[\frac{c_o^2}{c^2(x,t)} - 1 \right] \tag{226}$$

(d) Solution for Non-Conservative Chemical

An exponential decay factor is added to the modified source solution, giving

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x(t + t_d)}}\ e^{-\frac{x^2}{4\ e_x t}}\ e^{-kt} \tag{227}$$

and the mass distribution over an interval of 2x, centered at the spill location, becomes:

$$m(x,t) = m\ e^{-kt} \frac{\sqrt{t}}{\sqrt{t + t_d}}\ \mathrm{erf}\left(\frac{x}{\sqrt{4\ e_x t}} \right) \tag{228}$$

For the maximum concentration at any location x, the derivative of the concentration distribution with respect to time gives:

$$\frac{\partial c}{\partial t} = \left[\frac{x^2}{4\ e_x t^2} - \frac{1}{2(t + t_d)} - k \right] \cdot c(x,t) \tag{229}$$

The distance x at which $\frac{\partial c}{\partial t} = 0$ is expressed in terms of the time as:

$$\frac{x^2}{4\ e_x} = \frac{t^2}{2(t + t_d)} + k\ t^2 \tag{230}$$

For a given value of time and location as computed above, the concentration is obtained using the equation for c(x,t).

The distance x at which a specified concentration exists as a function of time can be obtained from:

$$x^2 = 4\ e_x t \left\{ \ln \left[\frac{m}{\sqrt{2\pi}\sqrt{2\ e_x(t + t_d)}\ c(x,t)} \right] - kt \right\} \tag{231}$$

For values of $t > 0$, this expression is zero for

$$\sqrt{t + t_d}\ e^{kt} = \frac{m}{\sqrt{2\pi}\sqrt{2\ e_x}\ c(x,t)} \tag{232}$$

and this gives the condition determining whether the concentration has the value c(x,t) at a location $x > 0$, at the value of time specified.

e. Approximate Analysis

A characteristic of the Gaussian distribution obtained for the instantaneous point source is that the length of the spreading of the dispersing mass is proportional to the standard deviation of the distribution. In an earlier subsection, it was shown, for the one-dimensional case, that 68 percent of the mass is contained within an interval, centered about the spill location, of 2σ, and 95 percent of the mass in an interval of 4σ. Since the standard deviation is a function of time, this characteristic can be used to treat the dispersing mass as if it were contained within a fixed length (1-D) or volume (3-D) which increases in size over time. The dimensions of the length or volume are taken to be proportional to the standard deviations.

The ratio of the total mass to the length or volume gives the average concentration within the length or volume as a function of time. Since the maximum of the Gaussian distribution occurs at the spill location and concentrations are initially zero for all $|x| > 0$, the average concentration during the early stages of dispersion will tend to give only a crude estimate of the distribution. However during the later stages of the dispersion, the Gaussian distribution becomes flatter and the average concentration can give a more realistic representation.

In particular, since the concentration obtained from a Gaussian or similar distribution is a function of the distribution of the dispersing mass, considering the mass to be evenly distributed over an interval or length will underestimate the peak concentration in the interval and overestimate the distance over which concentrations at the average value will exist. The overestimation will be diminished as the concentrations are reduced. An approximate analysis is useful therefore to obtain an upper bound for the distance over which concentrations in excess of any specified hazard level may exist, as well as a rough estimate of the magnitude of those concentrations.

Although this type of analysis has not been incorporated within the water dispersion model due to the potential significance in limit analysis, a few considerations are discussed in the following paragraphs. The one-dimensional simplification does not enhance the characterization, and this discussion deals with three dimensional volumes.

In three dimensions the Gaussian distribution is characterized by the standard deviations along each coordinate axis: $\sigma_x = \sqrt{2\, e_x t}$, $\sigma_y = \sqrt{2\, e_y t}$, $\sigma_z = \sqrt{2\, e_z t}$. The dispersing mass can then be characterized in terms of certain fractions of the spilled material being contained within a volume (ellipsoid) where the lengths of the semi-axes of the ellipsoid are taken in proportion to the standard deviations of the distribution.

Conservation of mass can be used to express the fraction of total mass as a function of distance, from the origin of the dispersing mass, where distance is expressed in terms of the standard deviations. In practice, the resulting volume integrals are not readily evaluated and further simplifications may be necessary. Taking the standard deviations as proportional to the lengths of the semi-axes of the ellipsoid, the volume (cut by the x-y plane for a spill at the surface of the water) is given by:

$$V(t) = \frac{N}{2} \cdot \frac{4}{3} \sigma_x \sigma_y \sigma_z \qquad (233)$$

where N is a constant of proportion determined from conservation of mass such that the amount of mass contained within the volume is expressed in terms of the total quantity discharged: $M(V) = r \cdot M$, r giving the fraction of total mass contained in V(t). The average concentration over this volume is obtained as:

$$\bar{c} = \frac{M(V)}{V(t)} = \frac{3 \cdot r \cdot M}{2\, N\, \sigma_x \sigma_y \sigma_z} \qquad (234)$$

The lengths of the semi-axes of the ellipsoid, $\sigma_x\sqrt[3]{N}$, $\sigma_y\sqrt[3]{N}$ and $\sigma_z\sqrt[3]{N}$, give the distance from the center of the dispersing mass for which this average concentration is determined. For a one-dimensional distribution, the equivalent value of r/N ranges from 0.39 for a semi-axis length of 0.2σ to nearly 0.24 at 2σ, and the approximate model will require calibration to determine an appropriate value of this ratio for the particular application. Since the peak concentrations, given by the Gaussian distribution, occur at the location of the spill, and are also inversely proportional to the product of the standard deviations, these values can be obtained as a function of time by a simple scaling of the average concentration. Conversely, the average concentrations can be scaled to obtain the distances for any desired fraction of the peak concentration.

For spills into moving water, the average concentration is obtained in a volume, centered at the center of mass of the spilled chemical but being translated in the direction of bulk fluid flow. The distances σ_x, σ_y, and σ_z are measured relative to the center of mass of the spill, and a linear translation is required to obtain distances in a coordinate system fixed relative to the moving water.

In the case of a river or similar body of water, where the dispersion of the spilled mass is constrained by flow boundaries such as the channel banks or bottom, the average concentration is computed over an ellipsoid volume only in the initial stages of unconfined dispersion. As the volume increases in size, further increase in size along one or more directions will become confined. As this occurs, the form of the expression for the volume, V(t), is changed and adaptation for the geometry of the particular water body is required.

For non-conservative substances, decaying or degrading over time according to a rate constant k, the total mass used to obtain the average concentration is $M \cdot e^{-kt}$ where M is the amount initially discharged.

4. CONTINUOUS SOURCES

Continuous spill models are characterized by a time-varying release of the spilled chemical, and continuous discharge conditions are described in Section I. As is the case for the instantaneous spill models, there are a number of different formulations possible for the continuous models and some of these are described in the following paragraphs using the one-dimensional case for simplicity. In general, the continuous spill models are expressed in terms using integrals of instantaneous spill solutions with respect to time; closed form solutions are not as readily obtained and numerical integration techniques are often used. Also the integral method permits solutions to be developed for any arbitrary time-varying discharge; however, in the following sections a constant discharge rate, $\dot{m}$, over a finite duration, 0 to t_{mt}, has been assumed.

a. Point Source

The method of obtaining a continuous point-source diffusion formula from solutions of the diffusion equation for instantaneous point sources proceeds according to the principle of superposition. The continuous release is regarded as being composed of an infinite number of overlapping instantaneous releases. That is, at any spatial position the concentration is given by the sum of the concentrations at that position from each of the instantaneous releases, with suitable adjustments in the difference between time of observation and time of release to account for the different release times of each instantaneous release. Mathematically, this corresponds to integration of the concentration for an instantaneous release with respect to time, where the integration limits are chosen depending on the duration of the continuous release.

Except for simplified cases, this integration is not analytically convenient because the values of σ, in general, depend on t, and for spills into moving bodies of water, on spatial coordinates since the origin of the center of the dispersing mass is translated by the water velocity (e.g., $x - x_o = u(t - t_o)$ in the case of one-dimensional flow). As a practical matter then, for one-dimensional bulk flow along the x-axis, diffusion along the x-axis is usually neglected by comparison with the gross transport along the x-axis by the mean water velocity u.

(1) Concentration Equation

For the one-dimensional case, the concentration resulting from an instantaneous point source is given by:

$$c(x,t) = \frac{m}{\sqrt{2\pi}\sqrt{2\, e_x t}}\, e^{-\frac{x^2}{4\, e_x t}} \qquad (235)$$

where m is the quantity of mass instantaneously discharged at $x = 0$, $t = 0$. For a continuous discharge at a constant rate, $\dot{m}$, the quantity discharged over a small interval of time $d\tau$ is $\dot{m}d\tau$, and this increment of the discharge is modeled using the instantaneous point source equations. The total concentration, resulting from the continuous discharge over a period of time 0 to τ, is then obtained by summing the contributions from each of these infinitesimal instantaneous sources, resulting in the integral expression for the continuous discharge:

$$c(x,t) = \int_0^{\tau_s} \frac{\dot{m}}{\sqrt{2\pi}\sqrt{2\, e_x(t - \tau)}}\, e^{-\frac{x^2}{4\, e_x(t-\tau)}}\, d\tau \tag{236}$$

The elapsed time of the instantaneous point source solution is written as $t-\tau$ to give the elapsed time from the incremental instantaneous spill, $\dot{m}d\tau$, at time τ to the observation time t, measured from 0 at the start of the continuous discharge. The limits of integration are written from the start of the continuous spill to a later time τ_s.

The value taken for the upper limit of integration depends on the nature of the discharge and the value of the observation time t:

> If the continuous discharge is assumed to emit indefinitely, then the limit of integration τ_s becomes ∞.
>
> If the continuous discharge is assumed to occur for a finite duration, t_{mt}, then the limit of integration is taken as $\tau_s = t$ for all observation times $t < t_{mt}$, and $\tau_s = t_{mt}$ for all observation times $t > t_{mt}$.

The integral is evaluated using a transformation

$$\beta = \frac{x}{2\sqrt{e_x}\sqrt{t - \tau}} \tag{237}$$

where β is defined by equation (237) as a transformation variable and is not to be confused with previous use.

This gives

$$\frac{d\tau}{\sqrt{t - \tau}} = \frac{x \, d\beta}{\sqrt{e_x} \, \beta^2} \tag{238}$$

and the integral becomes:

$$c(x,t) = \frac{\dot{m} \, x}{2\sqrt{\pi} \, e_x} \int_{\beta_0}^{\beta_s} e^{-\beta^2} \frac{d\beta}{\beta^2} \tag{239}$$

where

$$\beta_0 = \frac{x}{2\sqrt{e_x}\sqrt{t}}, \qquad \beta_s = \frac{x}{2\sqrt{e_x}\sqrt{t - \tau_s}} \tag{240}$$

Integration by parts gives:

$$\int_{\beta_0}^{\beta_s} e^{-\beta^2}\frac{d\beta}{\beta^2} = -\frac{1}{\beta}e^{-\beta^2}\Bigg|_{\beta_0}^{\beta_s} - 2\int_{\beta_0}^{\beta_s} e^{-\beta^2}\,d\beta$$

$$= -\frac{1}{\beta}e^{-\beta^2}\Bigg|_{\beta_0}^{\beta_s} - 2\int_0^{\beta_s} e^{-\beta^2}\,d\beta + 2\int_0^{\beta_0} e^{-\beta^2}\,d\beta \qquad (241)$$

where the integral from β_0 to β_s has been written in terms of the difference between two integrals, assuming $\beta_s > \beta_0$ which is only true if $x > 0$. If written for the case $x < 0$, the signs on the last two terms are reversed.

The integrals on the right hand side are error functions, so the expression for the concentration is obtained as:

$$c(x,t) = \frac{\dot{m}}{\sqrt{\pi\, e_x}}\left\{\sqrt{t}\, e^{-\beta_0^2} - \sqrt{t-\tau_s}\, e^{-\beta_s^2}\right\}$$

$$+ \frac{\dot{m}\,x}{2\,e_x}\left\{\operatorname{erf}(\beta_0) - \operatorname{erf}(\beta_s)\right\}, \qquad x > 0 \qquad (242)$$

(a) $t < t_{mt}$

The continuous discharge is assumed to occur over an interval of time from 0 to t_{mt}. If the observation time t is less than t_{mt}, then the upper limit of integration, τ_s, is equal to t. At this limit, $\beta_s \to \infty$, $\operatorname{erf}(\beta_s) \to 1$ and the equation for the concentration becomes:

$$c(x,t) = \frac{\dot{m}\sqrt{t}}{\sqrt{\pi\, e_x}}\, e^{-\frac{x^2}{4 e_x t}} + \frac{\dot{m}\,x}{2\,e_x}\left\{\operatorname{erf}\left(\frac{x}{2\sqrt{e_x}\sqrt{t}}\right) - 1\right\} \qquad (243)$$

(b) $t > t_{mt}$

When the observation time exceeds the duration of the continuous spill, then the upper limit of integration τ_s is equal to t_{mt} since the contribution of the instantaneous point sources after t_{mt} is zero. For $\tau_s = t_{mt}$,

$$\beta_s = \frac{x}{2\sqrt{e_x}\sqrt{t - t_{mt}}} \tag{244}$$

and the concentration is given by:

$$c(x,t) = \frac{\dot{m}}{\sqrt{\pi e_x}} \left\{ \sqrt{t}\, e^{-\frac{x^2}{4 e_x t}} - \sqrt{t - t_{mt}}\, e^{-\frac{x^2}{4 e_x (t - t_{mt})}} \right\}$$

$$+ \frac{\dot{m}\, x}{2 e_x} \left\{ \mathrm{erf}\left(\frac{x}{2\sqrt{e_x}\sqrt{t}} \right) - \mathrm{erf}\left(\frac{x}{2\sqrt{e_x}\sqrt{t - t_{mt}}} \right) \right\} \tag{245}$$

(2) Conservation of Mass

The total quantity of dispersing mass is obtained from the integral of the concentration over the distance x. Noting that the integration of the point source solution introduced a condition that $|x| \geq 0$, the mass distribution, over an interval of width 2x, centered at the spill origin is written as:

$$m(x,t) = 2 \int_0^x c(\beta,t)\, d\beta \tag{246}$$

Using the definition

$$\int \beta \ \mathrm{erf}(a\beta)\, d\beta = \frac{1}{2}\beta^2 \ \mathrm{erf}(a\beta) - \frac{1}{4a^2}\ \mathrm{erf}(a\beta) + \frac{\beta}{2a\sqrt{\pi}}\, e^{-a^2\beta^2} \tag{247}$$

the concentration integrals can be evaluated to give:

$$m(x,t) = \dot{m}\left(t + \frac{x^2}{2\ e_x}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{e_x t}}\right) + \frac{\dot{m}\ x\sqrt{t}}{\sqrt{\pi}\ e_x}\, e^{-\frac{x^2}{4\ e_x t}} - \frac{\dot{m}\ x^2}{2\ e_x}, \qquad t < t_{mt} \tag{248}$$

and,

$$\begin{aligned} m(x,t) = {} & \dot{m}\left(t + \frac{x^2}{2\ e_x}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{e_x t}}\right) \\ & - \dot{m}\left(t - t_{mt} + \frac{x^2}{2\ e_x}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{e_x}\sqrt{t - t_{mt}}}\right) \\ & + \left(\frac{\dot{m}\ x\sqrt{t}}{\sqrt{\pi}\ e_x}\right) e^{-\frac{x^2}{4\ e_x t}} - \left(\frac{\dot{m}\ x\sqrt{t - t_{mt}}}{\sqrt{\pi}\ e_x}\right) e^{-\frac{x^2}{4\ e_x (t - t_{mt})}}, \qquad t > t_{mt} \end{aligned} \tag{249}$$

In the limit as x → ∞, it can be seen that the first expression correctly reduces to $\lim_{x\to\infty} m(x,t) = \dot{m}\ t$, and the second gives $\lim_{x\to\infty} m(x,t) = \dot{m}\ t_m$.

(3) Behavior of Solution

The concentrations at the origin are obtained as:

$$c(0,t) = \frac{\dot{m}\sqrt{t}}{\sqrt{\pi\, e_x}}, \qquad t < t_{mt} \tag{250}$$

$$c(0,t) = \frac{\dot{m}}{\sqrt{\pi\, e_x}}\left[\sqrt{t} - \sqrt{t - t_{mt}}\right], \qquad t > t_{mt} \tag{251}$$

and the maximum value occurs at $t = t_{mt}$ to give:

$$c_{max} = \frac{\dot{m}\sqrt{t_{mt}}}{\sqrt{\pi\, e_x}} \tag{252}$$

Initially, the concentration at the origin is zero and then increases during the entire duration of release.

For values of $x > 0$, it can also be seen that if the duration of the release is very long, the solution for $t < t_{mt}$ produces concentrations which continually increase at all locations. The behavior of the one-dimensional solution for this source is very different from the behavior of the three-dimensional distribution in which steady state values are approached for large values of time.

5. METHOD OF DEVELOPING THREE-DIMENSIONAL SOLUTIONS

Solutions to the one-dimensional instantaneous point source problem were obtained in the form:

$$c(x,t) = \frac{a}{\sigma_x} e^{-\frac{x^2}{2\sigma_x^2}} \qquad (253)$$

and conservation of mass was applied to evaluate the coefficient a over the volume of the transporting fluid, giving $a = \frac{m}{\sqrt{2\pi}}$. Solutions to the partial differential diffusion equation, for a non-isotropic transporting fluid, are obtained in two or three dimensions as products of one-dimensional solutions. For example, the form of the concentration distribution for dispersion in a three-dimensional body of still water ($u = v = w = 0$), for a conservative substance ($k = 0$), from an instantaneous point source at the origin of the spatial coordinates on the surface of the water body, is obtained as the product of three one-dimensional instantaneous point source solutions:

$$c(x,t) = A \cdot \frac{1}{\sigma_x} e^{-\frac{x^2}{2\sigma_x^2}} \cdot \frac{1}{\sigma_y} e^{-\frac{y^2}{2\sigma_y^2}} \cdot \frac{1}{\sigma_z} e^{-\frac{z^2}{2\sigma_z^2}} \qquad (254)$$

where, as before, the constant coefficient A is determined from conservation of mass in the transporting fluid (and is found to be proportional to the total quantity of dispersing mass). Evaluation of the derivatives of this expression and substitution in the appropriate three-dimensional form of the diffusion equation demonstrates that this solution satisfies the governing partial differential equation. Since the basic form of the three-dimensional solution is very similar to the one-dimensional example described earlier, the behavior of the concentration distribution is also similar in many ways. However, the dispersion occurs much more rapidly since the products $\sigma_x^{-1} \cdot \sigma_y^{-1} \cdot \sigma_z^{-1}$ give a function of time of $t^{-3/2}$ as opposed to $t^{-1/2}$ for the one-dimensional case.

Since the integral of the concentration over the spatial volume leads to expressions requiring multiple integrations of error function arguments, conservation of mass (to determine the appropriate value of the coefficient A) is usually applied to an infinite or semi-infinite transporting volume. If physical boundaries, such as river channel banks, are present, solutions for confined flow are obtained by a method of imaging or using virtual sources to construct solutions by summing contributions from solutions for unconfined flow.

As was illustrated in the one-dimensional example, the principle of obtaining concentrations resulting from an instantaneous source distributed over a finite initial volume involves integration over that volume of the contributions from a series of instantaneous point sources. Except for very simply shaped volumes, it is extremely difficult to obtain closed form representations for these integrals.

For spills into bodies of water in which the velocity of bulk fluid flow is not zero, the center of mass of the spilled chemical experiences a bulk translation in the direction of fluid flow, and turbulent dispersion continues to occur relative to the moving center of mass. Thus, the transition from a still water model to a model for moving water requires only a simple mathematical transformation. For a spill into a non-tidal river, with flow in the direction of the x-axis at a constant velocity u, the center of mass at any time t is displaced from the original location by a distance ut.

If the coordinate x is referenced to the original spill location, then the separation along the x-axis between any observation point (at x) and the center of the dispersing mass becomes a function of time given by x - ut, and the form of the concentration distribution for an instantaneous point source release is immediately obtained as:

$$c(x,t) = A \cdot \frac{1}{\sigma_x} e^{-\frac{(x-ut)^2}{2\,\sigma_x^2}} \cdot \frac{1}{\sigma_y} e^{-\frac{y^2}{2\,\sigma_y^2}} \cdot \frac{1}{\sigma_z} e^{-\frac{z^2}{2\,\sigma_z^2}} \qquad (255)$$

Solutions for continuous releases in two or three dimensions for point or distributed sources are obtained using the principle of superposition by integrating contributions from appropriate instantaneous sources over time.

In reference[17] mention is made of earlier work in 1955 comparing various initial volume-source distribution functions with the initial Gaussian distribution. The conclusions from that study, although in reference to atmospheric dispersion, were that the Gaussian initial volume leads to much simpler diffusion equations and that it is conservative; that is, it leads to downwind concentrations slightly greater than for other volume-source distributions that were considered. Since the same equations are used for the formulation of the water dispersion models, these conclusions apply in this case as well.

SECTION III

MODELS FOR STILL WATER

1. INTRODUCTION

The model for the dispersion of a spilled chemical into a lake or ocean is based on simple three-dimensional diffusion in an unconstrained three-dimensional water body characterized by the absence of a bulk flow velocity component. The model does not include effects of thermally stratified layers in the water body, nor directly incorporate effects of wind or thermally induced currents. The water body is assumed to be non-isotropic, and the model is formulated assuming constant, but different, turbulent dispersion coefficients in each of the principal directions. Methods of developing estimates for the values of the turbulent dispersion coefficients are described, and the model is formulated to accept user provided input data if available. In the absence of user values, a method of automatically providing estimates of turbulent dispersion coefficients is developed using scaled values of molecular diffusion coefficients for diffusion in an ideal fluid.

2. GENERAL SOLUTION

As shown in Section II, the general form of the solutions to the diffusion equation in three dimensions is obtained as a product of three one-dimensional distributions:

$$c(x,y,z,t) = A \cdot \frac{1}{\sigma_x} e^{-\frac{x^2}{2\sigma_x^2}} \cdot \frac{1}{\sigma_y} e^{-\frac{y^2}{2\sigma_y^2}} \cdot \frac{1}{\sigma_z} e^{-\frac{z^2}{2\sigma_z^2}} \qquad (256)$$

where A is a constant to be determined from conservation of mass, and the standard deviations are:

$$\sigma_x = \sqrt{2\, e_x t}$$

$$\sigma_y = \sqrt{2\, e_y t}$$

$$\sigma_z = \sqrt{2\, e_z t} \qquad (257)$$

The dispersion coefficients e_x, e_y, e_z may, in general, be different in different directions, although often horizontal dispersion is assumed to be isotropic so that $e_y = e_x$.

The form of the concentration distribution given above applies for an instantaneous point source in the absence of decay ($k = 0$). It can be verified by substitution that this form of the concentration distribution satisfies the three-dimensional partial differential diffusion equation applicable for this type of water body ($u = v = w = 0$) and for any value of the coefficient A:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(e_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(e_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(e_z \frac{\partial c}{\partial z}\right) \qquad (258)$$

The decay coefficient, k, has been taken as zero only for simplicity in developing the form of the concentration distribution; subsequently, a decay term will be applied to the total quantity of dispersing mass.

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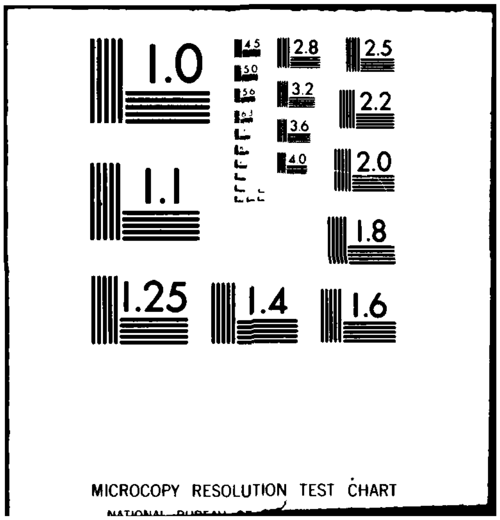
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MICROCOPY RESOLUTION TEST CHART

Conservation of mass requires that, in the absence of any sinks or sources, the total mass of a conservative substance dispersing in the environment at any time t be equal to the total mass of substance, M, originally released instantaneously at the spill location (x = 0). The total mass is obtained as the integral of the concentration over the volume of the receiving water body. Since the still water model assumes that the dispersion is unconvined, in the horizontal directions, the distances x and y extend infinitely in both directions from the spill location. The spill is assumed to occur on the surface of the water body, and the z coordinate (depth) extends from the surface (x = 0) to an infinite depth. This gives for the mass contained within a rectangular volume of length 2x and width 2y, centered at the spill location, and depth z below the surface:

$$M(x,y,z,t) = \frac{A}{\sigma_x \sigma_y \sigma_z} \int_0^z \int_{-y}^y \int_{-x}^x e^{-\frac{x^2}{2\sigma_x^2}} e^{-\frac{y^2}{2\sigma_y^2}} e^{-\frac{z^2}{2\sigma_z^2}} dx\, dy\, dz \quad (259)$$

The volume integration is simplified as a result of the rectangular shape, that is, the measure of length of the volume in each coordinate direction is independent of the values of the two remaining coordinates (this is not the case for example if the volume of an ellipsoid, intersected by the plane of the water surface, were used, with lengths of the semi-axes proportional to σ_x, σ_y, σ_z). Since the terms in each integrand are uncoupled, the evaluation of each integral proceeds directly using, from the definition of the error function:

$$\int_{-x}^{x} e^{-\frac{\tau^2}{2\sigma_x^2}} d\tau = 2\int_{0}^{x} e^{-\frac{\tau^2}{2\sigma_x^2}} d\tau = \sqrt{2\pi}\,\sigma_x \operatorname{erf}\left(\frac{x}{\sqrt{2}\,\sigma_x}\right) \qquad (260)$$

This gives for the mass distribution:

$$M(x,y,z,t) = \frac{A}{\sigma_x\,\sigma_y\,\sigma_z} \cdot \sqrt{2\pi}\,\sigma_x \operatorname{erf}\left(\frac{x}{\sqrt{2}\,\sigma_x}\right)$$

$$\cdot \sqrt{2\pi}\,\sigma_y \operatorname{erf}\left(\frac{y}{\sqrt{2}\,\sigma_y}\right) \cdot \frac{\sqrt{2\pi}}{2}\,\sigma_z \operatorname{erf}\left(\frac{z}{\sqrt{2}\,\sigma_z}\right) \qquad (261)$$

The standard deviations cancel, leaving the result:

$$M(x,y,z,t) = \frac{A(2\pi)^{3/2}}{2} \operatorname{erf}\left(\frac{x}{\sqrt{2}\,\sigma_x}\right) \cdot \operatorname{erf}\left(\frac{y}{\sqrt{2}\,\sigma_y}\right) \cdot \operatorname{erf}\left(\frac{z}{\sqrt{2}\,\sigma_z}\right) \qquad (262)$$

which gives a general expression for the total mass contained in the volume $z \cdot 2y \cdot 2x$ as a function of time.

As the dimensions of the volume are taken to be increasingly larger, the error function values approach the limit of 1, giving for the total mass in the system:

$$M = \lim_{\substack{x \to \infty \\ y \to \infty \\ z \to \infty}} M(x,y,z,t) = \frac{A}{2}\,(2\pi)^{3/2} \qquad (263)$$

where M is the amount of chemical initially introduced instantaneously at the spill location. The limit value reached for M(x,y,z,t) is not a function of time, satisfying mass conservation. The constant coefficient can now be determined in terms of the value of M as:

$$A = \frac{2M}{(2\pi)^{3/2}} \tag{264}$$

and the concentration distribution becomes:

$$c(x,y,z,t) = \frac{2M}{(2\pi)^{3/2}\,\sigma_x\,\sigma_y\,\sigma_z}\, e^{-\frac{x^2}{2\sigma_x^2}}\, e^{-\frac{y^2}{2\sigma_y^2}}\, e^{-\frac{z^2}{2\sigma_z^2}} \tag{265}$$

Substituting the expressions for the standard deviations in terms of time and the dispersion coefficients gives the final form of the concentration equation for an instantaneous source as:

$$c(x,y,z,t) = \frac{M}{4\,(\pi)^{3/2}\sqrt{e_x\,e_y\,e_z}\;t^{3/2}}\, e^{-\frac{x^2}{4e_x t}}\, e^{-\frac{y^2}{4e_y t}}\, e^{-\frac{z^2}{4e_z t}} \tag{266}$$

Further simplification, not taken here, can be introduced if the water body is assumed to be isotropic: $e_x = e_y = e_z$. The above form of the solution will produce infinite initial concentrations at the spill origin due to the appearance of $t^{3/2}$ in the denominator; however, these values will be rapidly reduced in time because of the value of the exponent, 3/2.

To obtain a solution for a non-conservative mass, decaying exponentially with a rate constant k, the mass M in the above formulation is replaced by Me^{-kt}.

3. INSTANTANEOUS SPILL MODEL

The Gaussian distribution obtained above gives the expression for the concentration distribution produced by an instantaneous release of a finite quantity of mass M at $t = 0$ and $x = y = z = 0$. The Gaussian distribution, however, cannot account for the initial volume distribution of the spilled mass, with the result that very large concentrations in excess of the density of the chemical will be obtained for small values of time and distance about the spill point.

The values computed from the Gaussian distribution can be artificially constrained such that $c(x,y,z,t)$ is less than the density ρ of the substance. However, it would be useful if a method could be adapted that would permit solutions for specified intital values of the concentration at the spill location.

Referring to Section II, the method of obtaining an integral solution for a distributed source appears promising, but the uncertainty of specifying the initial geometry of the volume is a disadvantage, as is the difficulty of evaluating the integrals which involve coupled terms for the most reasonable and realistic volume shapes. For this model, the non-zero initial concentration distribution produced by the method of virtual sources could be unrealistic in application if the initial concentrations far from the spill location reach too large a value. Although conservation of mass is not satisfied for the initial stages of dispersion, the modified source solution appears to be the preferred alternative and is incorporated in the model below. The discrepancy in the conservation of mass is roughly equivalent to an implied time dependency of release, which is not altogether unreasonable, and is also roughly analogous to the loss of mass in the point source solution if the computed concentrations are artifically constrained to be less than a limit value. The modified source solution also has another advantage in that, by manipulating the specified initial concentration value, the resulting distribution can be brought as close to that for a point source as desired.

The concentration at the origin from the instantaneous point source solution can be written as:

$$c(0,0,0,t) = \frac{M}{\frac{1}{2}\,(2\pi)^{3/2}\,\sigma_x\,\sigma_y\,\sigma_z} \tag{267}$$

so that the denominator can be expressed as the volume of an ellipsoid cut in half by the water surface ($V = \frac{1}{2} \cdot \frac{4}{3}$ abc) where the lengths of the semi-axes of the ellipsoid are given by 2.277 σ_x, 2.277 σ_y, and 2.277 σ_z. For very small values of time, the standard deviations are small, giving the effect of distributing the fixed amount of spilled mass M over a very small volume, producing large initial values of concentration at the origin.

A modification, adapted from Section II, sets a lower limit, V_o, for this volume, and the concentration at the origin is written as;

$$c(0,0,0,t) = \frac{M}{\frac{1}{2}\,(2\pi)^{3/2}\,\sigma_x\,\sigma_y\,\sigma_z + V_o} \tag{268}$$

The denominator now can be considered to represent a volume which has an initial vlue V_o and increases in size with time in proportion to $t^{3/2}$. As time increases, the additional term V_o will become negligible so that the concentration distribution will approach that for a point source. This formulation is slightly different than the one-dimensional case described in

Section II in that the initial volume is separated here, and the one-dimensional case provided the modification by means of a delay time. At $t = 0$ and for large values of time, each formulation gives the same result. For small values of time, however, the method used for the three dimensional spill model gives a slower rate of growth for the volume terms, thus producing larger values of concentration.

The value of the initial volume V_o is determined from a specified initial value of concentration at the spill location, $c(0,0,0,0) = c_o$:

$$V_o = \frac{M}{c_o} \tag{269}$$

Incorporating a decay term and writing the concentration equation in terms of the dispersion coefficients give the final form of the equation for instantaneous spills into still water as:

$$c(x,y,z,t) = \frac{M\,e^{-kt}}{4\,(\pi)^{3/2}\sqrt{e_x\,e_y\,e_z}\;t^{3/2} + M/c_o}\;e^{-\frac{x^2}{4\,e_x t}}\;e^{-\frac{y^2}{4\,e_y t}}\;e^{-\frac{z^2}{4\,e_z t}} \tag{270}$$

For a given set of spill conditions, the terms M, k, e_x, e_y, e_z and c_o are constants; the independent variables of the concentration distribution are x, y, z, t. To simplify the form of the equation, the following terms are introduced:

$$s = 4\ (\pi)^{3/2}\sqrt{e_x\ e_y\ e_z} \tag{271}$$

$$r^2 = \frac{x^2}{4\ e_x} + \frac{y^2}{4\ e_y} + \frac{z^2}{4\ e_z} \tag{272}$$

and with $V_o = M/c_o$, the concentration equation simplifies to

$$c(r,t) = \frac{M}{s\ t^{3/2} + V_o} \cdot e^{-kt}\ e^{-r^2 t^{-1}} \tag{273}$$

In this form, it can be seen that the three-dimensional instantaneous spill model differs from the one-dimensional case by the exponent of the time in the denominator (the one-dimensional case gave $t^{1/2}$).

This equation gives concentrations that have a finite value, $c_o = M/V_o$, at $r = t = 0$, are zero for all other values of r at $t = 0$, and are zero at all values of r as $t \to \infty$. The following paragraphs give analyses of the behavior of the distribution between these extremes.

a. Time History at the Origin

Since, for any value of elapsed time, the maximum concentration throughout the water body occurs at the spill location, the time history at the origin can be used to determine the total elapsed time during which concentrations above a specified limit can be expected to exist anywhere in the environment.

At the spill location, $x = y = z = 0$ which give $r = 0$, and the expression for the concentration at the origin as a function of time becomes:

$$c(r=0,t) = c(0,t) = \frac{M\,e^{-kt}}{s\,t^{3/2} + V_o} \qquad (274)$$

As t ranges from 0 to ∞, the concentration ranges from the initial value at the origin, $c_o = M/V_o$ to 0. Due to the presence of the decay term, this equation is not readily inverted to obtain elapsed time as a function of specified concentration level c(0,t). Plotting concentration versus time will, however, give a readily interpreted means of determing the maximum time over which concentrations in excess of any limit value will exist in the environment:

If the decay term is omitted, the equation can be inverted and gives:

$$t = \frac{1}{s^{2/3}} \left[\frac{M}{c(0,t)} - V_o \right]^{2/3} \qquad (275)$$

Since the decay reduces the total mass of dispersing substance more rapidly, the value of time obtained from this expression (with k = 0) is greater than the elapsed time (with k > 0) over which concentrations in excess of c(0,t) are sustained. The values of time obtained for k = 0 are useful to identify upper limits for values of time in cases with k > 0.

b. Time History at Point r

Since the concentrations at all values of $|x| > 0$, $|y| > 0$, $|z| > 0$ are initially zero, and are zero for very large values of elapsed time, then at any location (x, y, z), at some time after the spill occurs, the concentration observed increases to a maximum value and then decreases as further dispersion takes place. The maximum concentration, for coordinates of an observation point at x, y, z giving a fixed value of r, occurs when $\frac{\partial c}{\partial t} = 0$ for Equation (273) which leads to:

$$\frac{\partial c}{\partial t} = \left[\frac{r^2}{t^2} - k - \frac{3\ s\ \ t}{2\ (s\ t^{3/2} + V_o)} \right] \cdot c(r,t) \tag{276}$$

This expression, equated to zero, is not easily solved for values of time, although it could be graphically displayed. Instead, a simplification is examined for $V_o = 0$, $k = 0$, and in this case, the condition $\frac{\partial c}{\partial t} = 0$ occurs at

$$t = \frac{2}{3} r^2 \tag{277}$$

for any particular value of r. The influence of non-zero values of k and V_o make it difficult to interpret the actual time of maximum concentration from this value. However, the expression for $\frac{\partial c}{\partial t}$ can readily be solved for r^2:

$$r^2 = t^2 \left[k + \frac{3\ s \sqrt{t}}{2\ (s\ t^{3/2} + V_o)} \right] \tag{278}$$

For any value of time, this equation can be used to compute r which then gives the coordinates of an observation point where the maximum concentration occurs at the specified value of time. The value of the maximum concentration is obtained by substituting the values of r and t into the equation c(r,t). The time scale over which t is varied can be estimated from the time history of concentration at the origin.

At an observation point defined by r, at the time the concentration reaches a maximum value at r, the nature of the Gaussian distribution is such that the concentrations for all values of r beyond the observation point are less than the maximum value at r. Hence, the value of r also gives the maximum distance from the spill location at which concentrations in excess of the maximum at r can exist. The corresponding values of c(r,t) and r together give a profile of the maximum hazard extent. Although these are not readily inverted to use for specific values of c(r,t) or r, the form of the equation permits generating these values using t as the independent variable.

Since at any location, given a specific value of r corresponding to the observation point, the concentration increases with elapsed time from the start of the spill to a maximum value, then gradually decreases, the time history of the concentration at the observation point is of interest as is the length of time at that location for which a given concentration level will be exceeded. The concentration at the observation point is given as a function of time by the equation for c(r,t). The time of arrival and duration at r of concentrations in excess of a specified hazard level can then be obtained by interpolation from a graphical display of the time history. The requested hazard level should not be greater than the maximum concentration at the observation point, or, conversely, the location of the observation point should not be beyond the maximum extent of concentrations in excess of the hazard level.

In the above discussion, the spatial coordinates x, y, z were represented for simplicity as

$$r^2 = \frac{x^2}{4\, e_x} + \frac{y^2}{4\, e_y} + \frac{z^2}{4\, e_z} \tag{279}$$

and cases of interest include behavior along the x, y, z axes as well as at a specific observation point (x, y, z). For example, if $y = z = 0$, then $r^2 = \frac{x^2}{4\, e_x}$ and the concentration distribution becomes

$$c(x,t) = \frac{M\, e^{-kt}}{s\, t^{3/2} + V_o}\, e^{-\frac{x^2}{4\, e_x t}} \tag{280}$$

Families of concentration curves can be obtained showing the concentration distribution along the x-axis (or any other axis) at different times. The maximum value attained on each curve will also lie on the envelope of the maximum concentrations for the particular value of x.

Other computed results may be similarly obtained for values of r selected along other coordinate axes.

c. Extent of Hazard

The equation for the concentration c(r,t) can be inverted to solve for the equivalent distance at which a specified concentration will exist as a function of time:

$$r^2 = t \cdot \ln \left[\frac{M}{c(r,t) \cdot (s\, t^{3/2} + V_o)} \right] - kt^2 \tag{281}$$

By setting c(r,t) to a specified hazard level, different values of time can be used to express the distance over which concentrations exceed this value as a function of time. The character of the Gaussian distribution indicates that values of r^2 will initially increase with time until a point on the concentration envelope is reached; then the values of r^2 will be reduced until the time that the specified concentration exists only at the spill location ($r^2 = 0$). Since the spill is modeled as an instantaneous source, one root of this equation occurs at $t = 0$ for all values of r. The maximum duration of the spread in excess of the specified hazard level is obtained as the second root and is obtained from:

$$\ln \left[\frac{M}{c(r,t) \cdot (s\, t^{3/2} + V_o)} \right] - kt = 0 \tag{282}$$

and it can be seen that this is equivalent to the equation given earlier expressing the concentration at the spill location as a function of time.

Given the time the concentration at the origin reaches a particular hazard level, intermediate values of time can then be used to compute the distance r^2 over which the concentrations exceed the hazard level.

In the absence of decay, the equation for r^2 becomes:

$$r^2 = t \cdot \ln \left[\frac{M}{c(r,t) \cdot (s\, t^{3/2} + V_o)} \right] \qquad (283)$$

The maximum duration (k=0) over which concentrations in excess of c(r,t) exist anywhere is given using the equation for the time history at the origin as:

$$t_d = \frac{1}{s^{2/3}} \left[\frac{M}{c(r,t)} - V_o \right]^{2/3} \qquad (284)$$

which gives $r^2 = t \cdot \ln(1) = 0$. For a given value of c(r,t), the maximum value of r occurs at a value of time such that $\frac{\partial r}{\partial t} = 0$ which leads to:

$$\ln \left[\frac{M}{c(r,t)\ (s\, t^{3/2} + V_o)} \right] = \frac{3\, s\, t^{3/2}}{2\ (s\, t^{3/2} + V_o)} \qquad (285)$$

Substitution of the equation for c(r,t) enables a solution of this equation for the distance r^2 as a function of time, which, however, is independent of c(r,t). The solution in that form gives the value of r^2 at which a maximum concentration, not necessarily the desired hazard level, is reached as a function of time. As a result, interpolation between values of r, computed for times between 0 and t_d, will yield the maximum extent for the specified hazard.

Plotted displays of the hazard extent profiles, prepared for a specific hazardous concentration level, give the total time during which the concentrations in the environment exceed the hazard level, the maximum distance for which this occurs and, for smaller distances, the time period during which that level is exceeded.

4. CONTINUOUS SPILL MODEL

The method of obtaining solutions for the continuous release spill conditions involves integrating the instantaneous point source solutions with respect to time over the duration of release. General application of the principle of superposition for arbitrary release rate conditions is discussed in Section II.

a. Integral Equation

The still water model assumes that the release rate, $\dot{M}$, is constant. The spill starts at elapsed time t = 0 and stops at a later time, t_{mt}. To apply the principle of superposition, the appropriate instantaneous point source equation for three dimensions, with decay, is given by:

$$c(x,y,z,t) = \frac{M\,e^{-kt}}{4\,(\pi)^{3/2}\sqrt{e_x\,e_y\,e_z}\;t^{3/2}}\;e^{-\frac{x^2}{4\,e_x t}}\;e^{-\frac{y^2}{4\,e_y t}}\;e^{-\frac{z^2}{4\,e_z t}} \qquad (286)$$

In Section III, paragraph 2, it was shown that this form of the solution satisfies both the governing partial differential equation and conservation of mass throughout the receiving water body.

Considering the quantity of mass, M, discharged instantaneously, as a component, $\dot{M}\, d\tau$, of the mass being discharged continuously, the continuous spill model is obtained by adding the concentrations at the observation point from all the incremental releases. Since this gives an integral over time, the equation is simplified using the notation from the preceding section:

$$s = 4\ (\pi)^{3/2} \sqrt{e_x\ e_y\ e_z} \tag{287}$$

$$r^2 = \frac{x^2}{4\ e_x} + \frac{y^2}{4\ e_y} + \frac{z^2}{4\ e_z} \tag{288}$$

to obtain

$$c(r,t) = \int_0^{\tau_s} \frac{\dot{M}\ e^{-k(t-\tau)}\ e^{-\frac{r^2}{(t-\tau)}}}{s\ (t-\tau)^{3/2}}\, d\tau \tag{289}$$

where $(t-\tau)$ is used in the instantaneous source integrand to give the elapsed time from the release of an incremental quantity $\dot{M}\, d\tau$, at time τ, to the observation time of interest, t. It should be noted that the dimensions of r are $(\text{time})^{1/2}$.

The upper limit of integration is written as τ_s since the actual limit to be used depends on the relative values of the observation time, t, and the time the spill stops, t_{mt}. If t is less than t_{mt}, the integrand gives the incremental contributions from the continuous release for the complete history of the release from t = 0 to t, and the limit τ_s is given by t. If

t is greater than t_{mt}, then for values of τ greater than t_{mt}, at which time the spill ceases, the incremental releases do not contribute to the concentration distributions; the upper limit τ_s then becomes t_{mt}.

(1) Numerical Evaluation

The evaluation of the integral expression in equation (289) can be carried out numerically. For values of $t < t_{mt}$, the upper limit of integration τ_s is given by t and the portion of the integrand given by

$$\frac{e^{-\frac{r^2}{(t-\tau)}}}{(t-\tau)^{3/2}} \tag{290}$$

becomes equal to 0/0. Using a series expansion, it can be shown that as $\tau \to t$, in the limit, the value of the integrand approaches 0. It is necessary to use the limit value and not attempt to compute the value of the integrand at $\tau = t$. Also, if r is taken as zero, i.e., observation point at the spill location, then for time $t < t_{mt}$, the integrand becomes infinite as $\tau \to t$ and the solution obtains an infinite concentration at the spill location for all values of time less than t_{mt}. Therefore, the numerical integration is carried out only for values of $r > 0$. In addition, the form of this integral expression does not contain any adjustment to restrict the concentration at the spill location to finite values, so for values of $r > 0$, concentrations greater than those from modified solutions will be obtained.

(2) Analytical Evaluation

The integral for the concentration in equation (289) is transformed using $\xi = \dfrac{r}{\sqrt{t - \tau}}$ to obtain:

$$c(r,t) = \frac{2\,\dot{M}}{s\,r} \int_{\xi_0}^{\xi_s} e^{-\frac{k\,r^2}{\xi^2}}\, e^{-\xi^2}\, d\xi \tag{291}$$

where $\xi_0 = \dfrac{r}{\sqrt{t}}$ and $\xi_s = \dfrac{r}{\sqrt{t - \tau_s}}$. (292)

To complete the square for the expression in the exponent, the following relations are written:

$$\left(\xi + \frac{r\sqrt{k}}{\xi}\right)^2 = \xi^2 + \frac{k\,r^2}{\xi^2} + 2\,r\sqrt{k} \tag{293}$$

$$\left(\xi - \frac{r\sqrt{k}}{\xi}\right)^2 = \xi^2 + \frac{k\,r^2}{\xi^2} - 2\,r\sqrt{k} \tag{294}$$

and it can be seen that the sum of these terms is equal to twice the magnitude of the exponent in the integrand. Substitution gives the integral as:

$$c(r,t) = \frac{2\,\dot{M}}{s\,r} \int_{\xi_0}^{\xi_s} \frac{1}{2} \left[e^{2\,r\sqrt{k}}\, e^{-\left(\xi + \frac{r\sqrt{k}}{\xi}\right)^2} + e^{-2\,r\sqrt{k}}\, e^{-\left(\xi - \frac{r\sqrt{k}}{\xi}\right)^2} \right] d\xi \tag{295}$$

The integrand now contains two separate terms in the form of integrands of the error function. Forming the derivative of the error functions:

$$d\left[\operatorname{erf}\left(\xi + \frac{r\sqrt{k}}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\left(\xi + \frac{r\sqrt{k}}{\xi}\right)^2}\left(1 - \frac{r\sqrt{k}}{\xi^2}\right) d\xi \qquad (296)$$

$$d\left[\operatorname{erf}\left(\xi - \frac{r\sqrt{k}}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\left(\xi - \frac{r\sqrt{k}}{\xi}\right)^2}\left(1 + \frac{r\sqrt{k}}{\xi^2}\right) d\xi \qquad (297)$$

then multiplying the first expression by $e^{2\,r\sqrt{k}}$, the second by $e^{-2\,r\sqrt{k}}$ and summing gives:

$$e^{2\,r\sqrt{k}}\, d\left[\operatorname{erf}\left(\xi + \frac{r\sqrt{k}}{\xi}\right)\right] + e^{-2\,r\sqrt{k}}\, d\left[\operatorname{erf}\left(\xi - \frac{r\sqrt{k}}{\xi}\right)\right] =$$

$$\frac{2}{\sqrt{\pi}}\, e^{2\,r\sqrt{k}}\, e^{-\left(\xi + \frac{r\sqrt{k}}{\xi}\right)^2}\left(1 - \frac{r\sqrt{k}}{\xi^2}\right) d\xi$$

$$+ \frac{2}{\sqrt{\pi}}\, e^{-2\,r\sqrt{k}}\, e^{-\left(\xi - \frac{r\sqrt{k}}{\xi}\right)^2}\left(1 + \frac{r\sqrt{k}}{\xi^2}\right) d\xi \qquad (298)$$

Both exponentials on the right-hand side are equal to the term in the original integrand, and this expression becomes:

$$e^{2\,r\sqrt{k}}\, d\left[\operatorname{erf}\left(\xi + \frac{r\sqrt{k}}{\xi}\right)\right] + e^{-2\,r\sqrt{k}}\, d\left[\operatorname{erf}\left(\xi - \frac{r\sqrt{k}}{\xi}\right)\right] =$$

$$\frac{2}{\sqrt{\pi}}\, e^{-\xi^2 - \frac{k\,r^2}{\xi^2}}\left(1 - \frac{r\sqrt{k}}{\xi^2}\right) d\xi$$

$$+ \frac{2}{\sqrt{\pi}}\, e^{-\xi^2 - \frac{k\,r^2}{\xi^2}}\left(1 + \frac{r\sqrt{k}}{\xi^2}\right) d\xi \qquad (299)$$

The right-hand side reduces to $\frac{4}{\sqrt{\pi}} e^{-\xi^2 - \frac{k\, r^2}{\xi^2}} d\xi$ which is in the form of the original integrand. Substitution then yields the following integrable form for the concentration:

$$c(r,t) = \frac{2\,\dot{M}}{s\,r} \int_{\xi_0}^{\xi_s} \frac{\sqrt{\pi}}{4} \left\{ e^{2\, r\sqrt{k}}\, d\left[\operatorname{erf}\left(\xi + \frac{r\sqrt{k}}{\xi}\right)\right] + e^{-2\, r\sqrt{k}}\, d\left[\operatorname{erf}\left(\xi - \frac{r\sqrt{k}}{\xi}\right)\right]\right\} \tag{300}$$

Integration gives the complete analytical expression for the concentration as:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{2\,s\,r} \left\{ e^{2\, r\sqrt{k}} \left[\operatorname{erf}\left(\xi_s + \frac{r\sqrt{k}}{\xi_s}\right) - \operatorname{erf}\left(\xi_0 + \frac{r\sqrt{k}}{\xi_0}\right)\right] \right.$$

$$\left. + e^{-2\, r\sqrt{k}} \left[\operatorname{erf}\left(\xi_s - \frac{r\sqrt{k}}{\xi_s}\right) - \operatorname{erf}\left(\xi_0 - \frac{r\sqrt{k}}{\xi_0}\right)\right]\right\} \tag{301}$$

The remaining step is to substitute the values of the limits ξ_0 and ξ_s for the two cases of interest, $t < t_{mt}$ and $t > t_{mt}$.

(a) $t < t_{mt}$

When the observation time t is less than the duration of the continuous release, the upper limit of the original integral, τ_s, is equal to t. This gives $\xi_0 = \frac{r}{\sqrt{t}}$ and $\xi_s = \infty$. Substitution of these values for the error function arguments gives:

$$\operatorname{erf}\left(\xi_s + \frac{r\sqrt{k}}{\xi_s}\right) = 1 \tag{302}$$

$$\operatorname{erf}\left(\xi_0 + \frac{r\sqrt{k}}{\xi_0}\right) = \operatorname{erf}\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right) \tag{303}$$

$$\operatorname{erf}\left(\xi_s - \frac{r\sqrt{k}}{\xi_s}\right) = 1 \tag{304}$$

$$\operatorname{erf}\left(\xi_0 - \frac{r\sqrt{k}}{\xi_0}\right) = \operatorname{erf}\left(\frac{r}{\sqrt{t}} - \sqrt{kt}\right) \tag{305}$$

and the concentration distribution for $t < t_{mt}$ becomes:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{2\ s\ r}\left\{e^{2\ r\sqrt{k}}\left[1 - \operatorname{erf}\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right)\right]\right.$$

$$\left. + \ e^{-2\ r\sqrt{k}}\left[1 - \operatorname{erf}\left(\frac{r}{\sqrt{t}} - \sqrt{kt}\right)\right]\right\} \tag{306}$$

The steady state distribution can be obtained from this solution by taking the limit as $t \rightarrow \infty$.

$$\lim_{t\rightarrow\infty} c(r,t) = c(r) = \frac{\dot{M}\sqrt{\pi}}{s\ r}\, e^{-2\ r\sqrt{k}} \tag{307}$$

The first term in the expression for the concentration:

$$e^{2r\sqrt{k}}\left[1 - \operatorname{erf}\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right)\right] \qquad (308)$$

has an analytical limit of zero as either r or t becomes large, although for large values of r, the form of the product is not numerically stable. From Section II, paragraph 3.a (7).(e), the modified numerical approximation for the error function is obtained as:

$$\operatorname{erf}(x) = 1 - P(b,\eta)\, e^{-x^2} \qquad \text{for } x \geq 0 \qquad (309)$$

where η is given by $\frac{1}{1 + px}$ and varies from 1 to 0 as x ranges from 0 to ∞.

The polynomial $P(b,\eta)$ is obtained from Hasting's approximation and ranges in value from 1 at $x = 0$, to 0 as $x \to \infty$.

Letting $\eta_r = \dfrac{1}{1 + p\left(\dfrac{r}{\sqrt{t}} + \sqrt{kt}\right)}$, this form of the error function approximation is substituted to yield:

$$e^{2r\sqrt{k}}\left[1 - \operatorname{erf}\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right)\right] = e^{2r\sqrt{k}}\, P(b,\eta_r)\, e^{-\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right)^2}$$

$$= P(b,\eta_r)\, e^{-\frac{r^2}{t} - kt} \qquad (310)$$

In this form the exponential $e^{2r\sqrt{k}}$ has been removed, and the entire expression is obtained in the form of a stable decaying exponential.

By substitution, the preferred form of the concentration equation for $t < t_{mt}$ is obtained as:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{2\,s\,r}\left\{P(b,\eta_r)\, e^{-\frac{r^2}{t} - kt} + e^{-2\,r\sqrt{k}}\left[1 - \mathrm{erf}\left(\frac{r}{\sqrt{t}} - \sqrt{kt}\right)\right]\right\} \qquad (311)$$

In the limit as $r \rightarrow 0$, the concentration at the spill location is given by:

$$\lim_{r\to 0} c(r,t) = \frac{\dot{M}\sqrt{\pi}}{2\,s\,r}\left\{1 - \mathrm{erf}\ (\sqrt{kt}) + 1 - \mathrm{erf}\ (-\sqrt{kt})\right\} \qquad (312)$$

Since $\mathrm{erf}(-\sqrt{kt}) = -\mathrm{erf}(\sqrt{kt})$, the error function terms cancel, giving the concentration at the spill location to be independent of time and infinite as $\frac{\dot{M}\sqrt{\pi}}{s\,r}$. This suggests an appropriate modification of the continuous discharge *equations, in a form similar to that used for the instantaneous release* case, giving the equation for the concentration at the spill location as:

$$c(0,t) = \lim_{r\to 0} c(r,t) = \lim_{r\to 0} \frac{\dot{M}}{\frac{s\,r}{\sqrt{\pi}} + \dot{V}_o} \qquad (313)$$

The modification term is written as $\dot{V}_o$ and has dimensions of volume per unit time. The value of $\dot{V}_o$ is determined from a specified concentration at the origin, $c(r=0,t) = c_o$, which gives $\dot{V}_o = \dot{M}/c_o$.

The concentration field for $r \geq 0$ is then described by:

$$c(r,t) = \frac{\dot{M}/2}{\frac{s\,r}{\sqrt{\pi}} + \dot{V}_o}\left\{P(b,\eta_r)\, e^{-\frac{r^2}{t} - kt} + e^{-2\,r\sqrt{k}}\left[1 - \mathrm{erf}\left(\frac{r}{\sqrt{t}} - \sqrt{kt}\right)\right]\right\} \qquad (314)$$

which remains finite for all values of r, decreasing as r increases. As the values of r increase, the effect of the term $\dot{V}_o$ is diminished and the distribution field of a continuous point discharge is approached. Specifying large values of c_o will reduce $\dot{V}_o$ and, in turn, reduce the difference between the modified distribution and the point source values for smaller values of r.

(b) $t > t_{mt}$

When the observation time t is greater than the duration of the continuous release, the upper limit of the original integral, τ_s, is equal to t_{mt}. This gives $\xi_0 = \frac{r}{\sqrt{t}}$ and $\xi_s = \frac{r}{\sqrt{t - t_{mt}}}$. Substitution of the value for ξ_s in the appropriate error function arguments in the concentration equation gives:

$$\operatorname{erf}\left(\xi_s + \frac{r\sqrt{k}}{\xi_s}\right) = \operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} + \sqrt{k}\sqrt{t - t_{mt}}\right) \tag{315}$$

$$\operatorname{erf}\left(\xi_s - \frac{r\sqrt{k}}{\xi_s}\right) = \operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} - \sqrt{k}\sqrt{t - t_{mt}}\right) \tag{316}$$

and the concentration distribution for $t > t_{mt}$ becomes:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{2\,s\,r}\left\{e^{2\,r\sqrt{k}}\left[\operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} + \sqrt{k}\sqrt{t - t_{mt}}\right) - \operatorname{erf}\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right)\right]\right.$$

$$\left. + e^{-2\,r\sqrt{k}}\left[\operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} - \sqrt{k}\sqrt{t - t_{mt}}\right) - \operatorname{erf}\left(\frac{r}{\sqrt{t}} - \sqrt{kt}\right)\right]\right\} \tag{317}$$

As t becomes large, it can be shown that the concentrations vanish. For large values of r, however, the first term exhibits the same type of instability as before, and terms in the error function arguments become infinite at $t = t_{mt}$. Expanding the first term using the error function approximation polynomials gives, for

$$\alpha = \frac{r}{\sqrt{t - t_{mt}}} + \sqrt{k}\sqrt{t - t_{mt}} \tag{318}$$

$$\beta = \frac{r}{\sqrt{t}} + \sqrt{kt} \tag{319}$$

$$\begin{aligned} & e^{2 r\sqrt{k}}\left[\operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} + \sqrt{k}\sqrt{t - t_{mt}}\right) - \operatorname{erf}\left(\frac{r}{\sqrt{t}} + \sqrt{kt}\right)\right] \\ & = e^{2 r\sqrt{k}}\left[P(b,\eta_\beta)\, e^{-\beta^2} - P(b,\eta_\alpha)\, e^{-\alpha^2}\right] \\ & = P(b,\eta_\beta)\, e^{-\frac{r^2}{t}}\, e^{-kt} - P(b,\eta_\alpha)\, e^{-\frac{r^2}{t - t_{mt}}}\, e^{-k(t-t_{mt})} \end{aligned} \tag{320}$$

which is substituted to obtain the preferred form of the concentration equation. In addition, the same singularity is present at r=0, and the modification term $\dot{V}_o$ is inserted. These give:

$$c(r,t) = \frac{\dot{M}/2}{\frac{s\,r}{\sqrt{\pi}} + \dot{V}_o} \left\{ P(b,\eta_\beta)\, e^{-\frac{r^2}{t}} e^{-kt} - P(b,\eta_\alpha)\, e^{-\frac{r^2}{t - t_{mt}}} e^{-k(t-t_{mt})} \right.$$

$$\left. + e^{-2\,r\sqrt{k}} \left[\mathrm{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} - \sqrt{k}\sqrt{t - t_{mt}} \right) - \mathrm{erf}\left(\frac{r}{\sqrt{t}} - \sqrt{kt} \right) \right] \right\} \qquad (321)$$

In the limit as $r \to 0$, the argument $\frac{r}{\sqrt{t - t_{mt}}}$ of the error functions, at small values of r, is very large so that as $t \to t_{mt}$ the above equation gives the same distribution for all values of $r > 0$ as the equation for $t < t_{mt}$. At very small values of r, as the time t increases beyond t_{mt}, the argument $\frac{r}{\sqrt{t - t_{mt}}}$ rapidly becomes small, leading to a different form of the expression for the concentration at the spill site.

(3) Concentration at Spill Location

The integral equation giving the concentration at an observation point x,y,z, is determined by summing the concentrations at that point from a series of infinitesimal instantaneous releases occurring over the duration of the continuous release. If the observation point is taken at the origin, the following expression is obtained:

$$c(r=0,t) = \int_0^{\tau_s} \frac{\dot{M}\, e^{-k(t-\tau)}}{s\,(t-\tau)^{3/2}}\, d\tau \qquad (322)$$

in which τ_s is equal to t if $t < t_{mt}$, or is equal to t_{mt} if $t > t_{mt}$. Since the concentration at the origin is initially infinite for an instantaneous release, similar behavior is indicated for the continuous release.

Using a transformation $\xi = \sqrt{k}\sqrt{(t - \tau)}$ gives the integral in the form:

$$c(r=0,t) = - \frac{2\,\dot{M}\sqrt{k}}{s} \int_{\xi_0}^{\xi_s} e^{-\xi^2} \frac{d\xi}{\xi^2} \tag{323}$$

with $\xi_0 = \sqrt{kt}$, $\xi_s = \sqrt{k}\sqrt{t - \tau_s}$. Since $\xi_0 > \xi_s$, the order of integration is reversed, then integration by parts gives:

$$c(r=0,t) = - \frac{2\,\dot{M}\sqrt{k}}{s\,\xi} e^{-\xi^2} \Bigg|_{\xi_s}^{\xi_0} - \frac{4\,\dot{M}\sqrt{k}}{s} \int_{\xi_s}^{\xi_0} e^{-\xi^2}\, d\xi \tag{324}$$

The remaining integral is obtained using error functions for integrals over the ranges 0 to ξ_0, and 0 to ξ_s, giving the concentration at the spill location in the form:

$$c(r=0,t) = \frac{2\,\dot{M}\sqrt{k}}{s} \left[\frac{1}{\xi_s} e^{-\xi_s^2} - \frac{1}{\xi_0} e^{-\xi_0^2} \right] + \frac{2\,\dot{M}\sqrt{k}\sqrt{\pi}}{s} \Big[\mathrm{erf}(\xi_s) - \mathrm{erf}(\xi_o) \Big] \tag{325}$$

If the observation time t is less than the duration of release, t_{mt}, then the original upper limit of integration τ_s is equal to t. This gives the value of ξ_s as zero, and the concentrations at the origin expressed by this equation are infinite for $t < t_{mt}$.

For values of $t > t_{mt}$, the upper limit of integration τ_s is equal to t_{mt}, and substitution gives:

$$c(r=0,t) = \frac{2\dot{M}}{s}\left[\frac{e^{-k(t-t_{mt})}}{\sqrt{t-t_{mt}}} - \frac{e^{-kt}}{\sqrt{t}}\right] + \frac{2\dot{M}\sqrt{k}\sqrt{\pi}}{s}\left[\operatorname{erf}\left(\sqrt{k}\sqrt{t-t_{mt}}\right) - \operatorname{erf}\left(\sqrt{kt}\right)\right] \qquad (326)$$

If the decay coefficient is zero, this equation reduces to the same result derived for a conservative substance.

For values of $t > t_{mt}$, this equation gives $c(r=0,t) \to \infty$ as $t \to t_{mt}$. For large values of t, using the approximation for large arguments of the error function shows that the concentrations identically reduce to zero.

To compensate for the behavior as $t \to t_m$, the term $\sqrt{t - t_{mt}}$ is factored out, and a constant term added to the denominator to give $c(r,t) = c_o$ as $r \to 0$. This gives the result:

$$c(r=0,t) = \left\{ \frac{2\,\dot{M}}{s\sqrt{t}\sqrt{t - t_{mt}} + \frac{2\,\dot{M}\sqrt{t_{mt}}}{c_o}} \right\} \cdot \left\{ \sqrt{t}\,e^{-k(t-t_{mt})} - \sqrt{t-t_{mt}}\,e^{-k\,t_{mt}} + \sqrt{k}\sqrt{\pi}\sqrt{t}\sqrt{t - t_{mt}}\left[\operatorname{erf}\left(\sqrt{k}\sqrt{t - t_{mt}}\right) - \operatorname{erf}\left(\sqrt{kt}\right)\right]\right\} \tag{327}$$

(4) Steady-State Distribution

If the continuous discharge emits indefinitely, the concentrations at different distances from the spill location will reach constant steady-state values. For any discharge of finite duration, the concentrations will approach, but not exceed, steady-state values as the duration increases. Thus, the steady-state concentration distribution gives the maximum concentrations that can be reached for a continuous discharge at rate $\dot{M}$.

The steady-state distribution is obtained from the concentration equation, Equation (306), in the range $t < t_{mt}$, in the limit as $t \to \infty$ as:

$$c(r) = \frac{\dot{M}\sqrt{\pi}}{s\ r}\ e^{-2\ r\sqrt{k}} \tag{328}$$

The concentration distribution is written as c(r) to indicate steady-state behavior. The steady-state distribution gives infinite concentrations at the spill location, r=0. At values $r > 0$, the steady-state concentrations diminish rapidly according to $\frac{1}{r}\,e^{-2\ r\sqrt{k}}$. It can be seen that the steady-state distribution is proportional to $\frac{\dot{M}}{s\ r}$ and that as $r \to 0$ the reciprocal of this term produces infinite concentrations at the spill location, so the equation is written as:

$$c(r) = \frac{\dot{M}}{\frac{s\ r}{\sqrt{\pi}} + \dot{V}_o} e^{-2\ r\sqrt{k}} \tag{329}$$

For a continuous discharge, emitting indefinitely, with decay, it can be seen from the discharge equations given in Section I that the total quantity of mass dispersing in the environment is constant, given by $\dot{M}/k$. The apparent distribution of a fixed amount of substance over a volume vanishing to a point at the spill location is analogous to the instantaneous point source behavior.

The steady-state equation can be used to obtain values of the concentration at different distances from the spill location, using the coordinates of the observation point (x, y, z) to obtain the appropriate value of r for each point. The equation is not readily inverted to obtain r in terms of c(r), so interpolation is required to determine the maximum hazard extent for a given hazard level.

Since the steady-state distribution gives an upper limit for indefinite discharges, the integral expression for a finite discharge should be used to obtain the concentration time history at any location to assess the relative magnitude of actual concentrations to the steady-state values.

b. Evaluation for Conservative Chemicals

In the absence of decay (k=0), the integral expression for the concentration as a function of time and distance becomes:

$$c(r,t) = \int_0^{\tau_s} \frac{\dot{M}\, e^{-\frac{r^2}{(t-\tau)}}}{s\,(t-\tau)^{3/2}}\, d\tau \qquad (330)$$

The concentration distributions obtained from this expression are simpler to evaluate than using the general equations for non-conservative substances, give an upper limit of concentrations, and provide limited independent verification of the formulation of the equations for non-conservative chemicals.

Applying the transformation:

$$\xi = \frac{r}{\sqrt{t - \tau}} \qquad (331)$$

obtains

$$c(r,t) = \frac{2\,\dot{M}}{s\,r} \int_{\xi_0}^{\xi_s} e^{-\xi^2}\, d\xi \qquad (332)$$

where $\xi_0 = \frac{r}{\sqrt{t}}$, $\xi_s = \frac{r}{\sqrt{t - \tau_s}}$

The limits of integration are separated to give:

$$c(r,t) = \frac{2\,\dot{M}}{s\,r} \int_0^{\xi_s} e^{-\xi^2}\, d\xi - \frac{2\,\dot{M}}{s\,r} \int_0^{\xi_0} e^{-\xi^2}\, d\xi \qquad (333)$$

and the evaluation is completed using the error function to obtain:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{s\ r}\left[\mathrm{erf}(\xi_s) - \mathrm{erf}(\xi_0)\right] \tag{334}$$

This expression can then be evaluated by substituting the values of the limits ξ_0 and ξ_s for the two cases of interest, $t < t_{mt}$ and $t > t_{mt}$.

(1) $t < t_{mt}$

For $t < t_{mt}$, then $\tau_s = t$. The upper limit $\xi_s = \infty$ and the error function $\mathrm{erf}(\xi_s) = 1$, giving:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{s\ r}\left[1 - \mathrm{erf}\left(\frac{r}{\sqrt{t}}\right)\right] \tag{335}$$

The steady-state distribution can be obtained from this solution by taking the limit as $t \to \infty$:

$$\lim_{t\to\infty} c(r,t) = c(r) = \frac{\dot{M}\sqrt{\pi}}{s\ r} \tag{336}$$

Since the steady-state distribution gives infinite concentrations as $r \to 0$, the equation is modified as before to obtain:

$$c(r) = \frac{\dot{M}}{\frac{s\ r}{\sqrt{\pi}} + \dot{V}_o} \tag{337}$$

The equation for $c(r,t)$ can be seen to be expressed in terms of the product of the steady-state value and a function of r and t which varies from 0 to 1. In the limit as $r \to 0$, the equation gives infinite concentrations at the origin, and a similar modification is:

$$c(r,t) = \frac{\dot{M}}{\frac{s\,r}{\sqrt{\pi}} + \dot{V}_o}\left[1 - \operatorname{erf}\left(\frac{r}{\sqrt{t}}\right)\right] \tag{338}$$

In the limit as r → 0 this expression gives $\lim_{r\to 0} c(r,t) = \frac{\dot{M}}{\dot{V}_o} = c_o$, and as t → ∞ the steady-state distribution is obtained.

(2) $t > t_{mt}$

For $t > t_{mt}$, then $\tau_s = t_{mt}$ and the concentration is obtained from Equation (334) as:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{s\,r}\left[\operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}}\right) - \operatorname{erf}\left(\frac{r}{\sqrt{t}}\right)\right] \tag{339}$$

As t becomes large, the error function terms approach zero and the concentrations vanish. Also, for large values of r, the concentrations become small. The numerical instability observed for $k > 0$ does not occur.

For very small values of r, as $t \to t_{mt}$, the value of the first error function term approaches 1 giving at time t_{mt}:

$$c(r,t_{mt}) = \frac{\dot{M}\sqrt{\pi}}{s\,r}\left[1 - \operatorname{erf}\left(\frac{r}{t_{mt}}\right)\right] \tag{340}$$

which is the same equation as obtained for $t < t_{mt}$. For finite concentrations at the origin, this equation for $t > t_{mt}$ is written as:

$$c(r,t) = \frac{\dot{M}}{\frac{s\,r}{\sqrt{\pi}} + \dot{V}_o} \left[\operatorname{erf}\left(\frac{r}{\sqrt{t - t_{mt}}} \right) - \operatorname{erf}\left(\frac{r}{\sqrt{t}} \right) \right] \tag{341}$$

For $r > 0$ and $t \sim t_{mt}$, the argument of the first error function is very large, giving the asymptotic value of 1 for all r as $t \to t_{mt}$. At $t = t_{mt}$ and as $r \to 0$, the concentration should be obtained as c_o. However, as t increases beyond t_{mt}, for very small values of r, the argument of the first error function rapidly becomes small, giving the behavior near the spill site as:

$$c(r,t) = \frac{2\,\dot{M}}{s} \left[\frac{1}{\sqrt{t - t_{mt}}} - \frac{1}{\sqrt{t}} \right] \tag{342}$$

where the unmodified solution obtains concentrations independent of r and having infinite values as $t \to t_{mt}$. Combining the fractions, the expression is limited to $c(r,t) = c_o$ as $t \to t_{mt}$ by writing:

$$c(0,t) = \frac{2\,\dot{M}\left[\sqrt{t} - \sqrt{t - t_{mt}}\right]}{s\sqrt{t}\sqrt{t - t_{mt}} + 2\,\dot{M}\sqrt{t_{mt}}/c_o} \tag{343}$$

(3) Steady State Distribution

In the absence of decay, the solution obtained for the concentration distribution is given by:

$$c(r,t) = \frac{\dot{M}\sqrt{\pi}}{s\,r} \left[1 - \operatorname{erf}\left(\frac{r}{\sqrt{t}} \right) \right] \tag{344}$$

for $t < t_{mt}$. In the limit as $t \to \infty$, then also $t_{mt} \to \infty$, and the concentrations are obtained for a source emitting continuously at a steady rate. As $t \to \infty$, the value of the error function term goes to zero, and the following steady-state concentration distribution is obtained:

$$c(x,y,z) = \frac{\dot{M}\sqrt{\pi}}{s\ r} = \frac{\dot{M}}{2\ \pi\sqrt{e_x\ e_y\ e_z}\ \sqrt{\frac{x^2}{e_x} + \frac{y^2}{e_y} + \frac{z^2}{e_z}}} \tag{345}$$

At any distance, x, y, z,or r, this expression gives the maximum concentration that will be attained for an infinitely long continuous release of a conservative substance.

Since the conditions of a release of finite duration and of a non-conservative substance both act to produce smaller concentrations, the steady-state value represents a maximum value but not necessarily an accurate estimate of the expected value. The major advantage is that a simple analytical expression is obtained relating maximum concentration and distance so that the general area of hazard extent can be approximately, but quickly, determined.

As might be expected since the continuous source solution was obtained by integration of an instantaneous point source solution, for very small distances from the spill location very large concentrations will be estimated. Since practically the concentrations at the spill location should remain finite, at some specified value c_o, a modification is applied to the steady-state equation to obtain:

$$c(x,y,z) = \frac{\dot{M}}{2\,\pi\sqrt{e_x\,e_y\,e_z}\sqrt{\frac{x^2}{e_x} + \frac{y^2}{e_y} + \frac{z^2}{e_z}} + \dot{V}_o} \tag{346}$$

where the notation $\dot{V}_o$ is used for the additional term since the dimensions are (volume/time). The value to be used for $\dot{V}_o$ is obtained from the initial value c_o as:

$$\dot{V}_o = \frac{\dot{M}}{c_o} \tag{347}$$

As the distance from the spill location increases, the effect of the modification will be diminished. The estimated concentrations will be less than, but approaching, those values obtained from the continuous point source solutions.

(a) Extent of Hazard

For illustration, setting $y = z = 0$, gives the following expression for the steady-state concentration as a function of distance x:

$$c(x) = \frac{\dot{M}}{2\,\pi\,x\sqrt{e_y\,e_z} + \dot{V}_o} \tag{348}$$

This is readily solved for the distance x, giving:

$$x = \frac{M - c(x)\,\dot{V}_o}{2\,\pi\,c(x)\sqrt{e_y\,e_z}} \tag{349}$$

This equation obtains the maximum distance x, over which concentrations greater than, or equal to, c(x) will exist under the conditions of steady-state continuous release, no decay, and values of c(x) less than c_o and greater than zero.

The effect of the value of $\dot{V}_o$ can be seen to reduce the maximum distance x over which concentrations will exceed c(x). By manipulating the specified initial value c_o, different values of $\dot{V}_o$ will be obtained; if c_o is very large, the values of x obtained from this equation will increase toward the point source solution values.

5. EVALUATION OF DISPERSION COEFFICIENTS

Turbulent mixing in lakes and in much of the shallower ocean areas is controlled by local wind forcing. Horizontal spreading may be more or less uniform, but vertical turbulent dispersion may be strongly diminished by ambient density stratification. As a result, the water body cannot be treated as a homogeneous media, dispersing a pollutant equally in the horizontal and vertical directions. However, it is difficult to obtain quantitative estimates for the horizontal dispersion coefficients, although experimental and theoretical work does suggest a somewhat more definitive formulation for estimates of vertical dispersion coefficients.

The nature of the water body stratification and methods for obtaining estimates of the turbulent dispersion coefficients are described in the following sections. In cases where insufficient data is available or estimates cannot be made, the following subsection describes the computation of molecular diffusion coefficients. Under proper scaling, which is also difficult to determine, the diffusion coefficients can be used in the absence of definitive descriptions for the particular water body.

a. Turbulent Dispersion

(1) Water Body Stratification

Lakes and reservoirs display seasonal temperature cycles that have significant effect on the diffusion of a spilled chemical.

In temperate zones, lakes are in an isothermal condition in the spring, that is, the water temperature is approximately uniform throughout the depth of the water body. By about late March, the water near the surface begins to warm so that by summer, the lake has become stratified and mixing does not readily occur among the layers.

The upper layer of the lake is known as the epilimnion and contains warmer water at an approximately uniform temperature. The epilimnion is well-aerated and well-mixed. Below the epilimnion is a usually narrow layer, the metalimnion, in which the water temperature decreases rapidly with depth. The thermocline is the point within the metalimnion at which the temperature gradient is a maximum. Below the metalimnion, the lower stratum is the hypolimnion in which the water remains cold throughout the year. The hypolimnion is stagnant, receiving nutrients expelled by the biota in the epilimnion and contains mostly anaerobic forms of life.

Sometime during the fall, as the lake begins to cool, the upper regions cool most rapidly. The density of the surface water increases above that of deeper water, and significant mixing occurs throughout the epilimnion as the surface water is caused to sink. Toward late fall, the lake has again reached an isothermal condition, with uniform temperature and density throughout. In this state, surface winds are particularly significant and, during this period of instability, can exert sufficient influence to cause complete turnovers of the lake water. This condition exists throughout the winter and into the spring when the heating process again occurs to establish the stable thermal stratifications.

In contrast to lakes in temperature zones with seasonal thermoclines, oceans have both permanent and seasonal thermoclines. The permanent thermocline exists from the equator north or south to about 60°N or S latitude. Further north or south the entire water column is cold. The maximum depth of the permanent thermocline occurs in the vicinity of 30° to 35° N or S latitude; depths are shallower at the equator. The uppermost region of the water layer in which rapid decrease in temperature occurs lies within the first several hundred feet to not more than about 1,000 feet from the surface. The seasonal thermocline is caused by temperature increases during the warmer months at shallower water depths, occurs in the temperate and tropical zones, and may lie at depths not greater than 500 feet.

The rate of turbulent dispersion is strongly influenced by the density gradients within the receiving water body. Near a thermocline, in a layer in which temperature changes occur rapidly with depth, the turbulent dispersion coefficients are low. Higher values of the coefficients occur at depths both above and below this layer; however, the hypolimnion has dispersion rates that are one or two orders of magnitude smaller than those found in the epilimnion[26]. For spills on the surface, the thermocline, in effect, acts as a constraint, limiting the extent to which dispersion to greater depths occurs.

(2) Vertical Dispersion Coefficient

Experimental evidence indicates that the vertical rate of turbulent dispersion in the water region below the surface and above the thermocline is related to the density gradient. Large density gradients reflect a stable water column, and low turbulent dispersion coefficients. As the density gradient becomes smaller, the turbulent dispersion coefficient increases.

An empirical expression[27] relating vertical diffusivity to the density gradient, which generally agrees well with available field data, is given by:

$$e_z = \frac{10^{-4}}{\Omega} \tag{350}$$

where e_z is the vertical dispersion coefficient in cm^2/second, and Ω is the density gradient in units of m^{-1}. Available data suggests values of the turbulent dispersion coefficient in this region of the water body in the range 0.1 to 100 cm^2/second, where values at the low end of this scale occur at the thermocline. Because of the temperature variation, the coefficient of vertical dispersion is actually a function of depth.

The density gradient Ω is given, in terms of the density, by

$$\Omega = \left| \frac{1}{\rho} \frac{d\rho}{dz} \right| \tag{351}$$

The stability of the water column, and therefore the density gradient, can be expressed by the Brunt-Vaisalla frequency:

$$N = \sqrt{g \, \Omega} \tag{352}$$

where g is the gravitational constant and the dimension of N is time^{-1}.

Near the surface of the water body, the density gradient may become extremely small, and the relationship between the vertical turbulent dispersion coefficient and the density gradient becomes invalid. In this case the dispersion is governed by wind and wave action. Figure 19 reproduces a diagram appearing in reference[27] suggesting a relationship between the vertical turbulent dispersion coefficient at the surface and the sea state. This figure shows values of the dispersion coefficient at the surface in the range of 100 to 300 cm^2/second, up to two orders of magnitude greater than the values at the thermocline.

Kullenberg, et al[28] have shown that vertical diffusivity can be related to the stratification of water, current shear, and wind speed such that

$$e_z = cW^2N^{-2} \; |dq/dz| \tag{353}$$

where c is a constant, W is the wind speed, N is the Brunt-Vaisalla frequency, and $|dq/dz|$ is the absolute value of the vertical current shear. For constant winds of 4-5 m/sec, the vertical mixing in the top 20 meters can be shown[28] to be:

$$e_z = c \; 10^{-8} \; \overline{W}^2 \; \overline{N}^{-2} \; |\overline{dq/dz}| \tag{354}$$

where the constant c ranges from 2 to 8, $\overline{W}^2$ is the mean square of the wind speed, $\overline{N}^2$ is the mean of the Vaisalla frequency, and $|dq/dz|$ is the mean shear. The value of c will tend toward the lower value for lakes and range to the higher value for oceans.

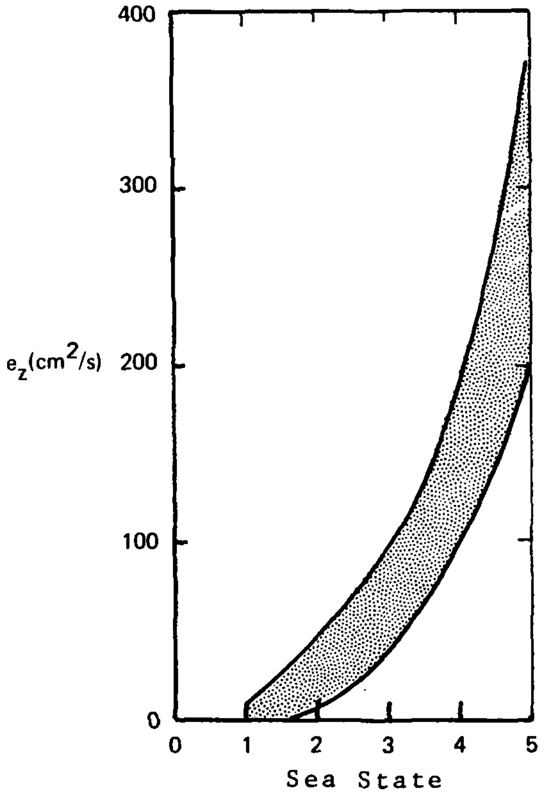

Figure 19. Relationship of Vertical Dispersion Coefficient to Sea State

For smaller or more variable winds, a different relationship will hold due to the fact that mixing is now more dependent upon local processes than upon winds. The source of energy is now due to kinetic energy fluctuations. To express this, Kullenberg, et al[29] found that:

$$e_z = 4.1 \times 10^{-4} \bar{q}^2 (\bar{N}^2)^{-1} |\overline{dq/dz}| \tag{355}$$

where $\bar{q}^2 = \bar{U}^2 + \bar{V}^2$, the current fluctuations. According to Kullenberg, this relationship can be applied to the hypolimnion.

Unfortunately, these expressions require data which cannot be expected to be available for the intended use of the spill model. An alternative formulation[30], which does not incorporate the effects of stratification, has been given as:

$$e_z = 2.75 \times 10^{-4} \frac{W^3}{g} \tag{356}$$

where W is the wind velocity at the surface of the water and g is the gravitational constant. Values obtained for e_z for several different wind speeds are given below:

Wind Speed		Dispersion Coefficient
Miles/Hour =	cm/sec	e_z, cm^2/sec
0	0	0
5	223.5	3.
10	447.0	25.
15	670.5	84.
20	894.0	200.
25	1117.5	391.

Different methods of obtaining vertical dispersion coefficients have been compared[30] under ranges of typical environmental conditions and were found to yield comparable values for e_z. The above expression is preferred for the water dispersion model due to the simplicity of obtaining an estimate of the dispersion coefficient from the wind velocity.

However, if the wind velocity is quite small, then the dispersion coefficient computed using the wind velocity may be less than that even at the thermocline. In this case the value of the dispersion coefficient can be contrained to be greater than some multiple of a computed molecular diffusion coefficient.

The water dispersion model as presently implemented assumes that the dispersion coefficient e_z does not substantially vary with depth, and a constant value is used. This is a reasonable assumption for mixing occurring in the upper layer of the water body but becomes more approximate as the dispersion spreads to greater depths.

The effect of the presence of a thermocline can be modeled by assuming an impenetrable boundary, with a user value to specify the depth to the thermocline. Inclusion of a virtual source term in the model would be required to reflect the spreading mass back into the upper layers of the water body. At present, the dispersion model does not include a thermocline boundary, and model calculations indicating dispersion occurring to depths over several hundred feet should be viewed quite cautiously.

(3) Horizontal Dispersion Coefficient

In lakes and on the continental shelf, horizontal turbulent dispersion is nearly isotropic, that is, $e_x = e_y$, and these regions (excluding shallow parts of the ocean dominated by tidal currents) exhibit several hydrodynamic similarities, including the fact that most of the kinetic energy of currents is derived from wind forcing. As a result, expressions for horizontal diffusivity can be applied in both regions, however, estimates of the coefficient values are difficult to obtain.

Theoretical work by Csanady [31] has showed that the horizontal diffusion coefficient, e_x, can be taken as:

$$e_x \propto \frac{\mu'}{L^{1/3}} \ell^{4/3} \tag{357}$$

where μ' = characteristic eddy velocity fluctuation

L = length scale of the turbulent eddies

and ℓ = length scale characterizing the size of the diffusing cloud

This expression can also be written as:

$$e_x = a\ L^{4/3} \tag{358}$$

where a is a dissipation parameter of units $cm^{2/3}$ per second and L is a measure of the spreading, usually taken as $4\ \sigma_x$. Experimental data suggests that the values of a are in the range of 10^{-2} to 10^{-4} $ft^{2/3}$/second, although compensation for the effects of shear currents suggests that the lower value of 10^{-4} may be most appropriate [27].

Csanady later showed that the standard deviation, σ, is proportional to the eddy velocity fluctuation, the time, and the length such that:

$$\sigma^2 \propto (\mu'\ t)^3/L \tag{359}$$

The strong relationship between the diffusion time, t, and the variance σ^2 is interesting due to the fact that t may vary over four orders of magnitude, creating a variation in σ^2 over 12 orders of magnitude. On the other hand, the effect of variation of the turbulent intensity indicated by μ' on σ^2 appears to be relatively slight.

Experimental research by Okubo [32] has shown the relationship between σ^2 and t to be slightly different from Csanady's theoretical equation. Okubo found that

$$\sigma^2 \propto t^{2.3} \tag{360}$$

which differs slightly from the t^3 shown by theory, and indicates that the dispersion coefficient e_x is proportional to $t^{1.3}$. It should be noted that this only expresses a relationship between e_x and time or dispersion length, but not an equation for use in computing e_x.

An alternative solution has been suggested by Schwab and Katz [33]. Based on experimentation in Lake Michigan, they describe lake diffusion in terms of a second order partial differential equation. Although their model may be sound, its complexity would require a prohibitive amount of computer time.

Csanady[31] suggests that in a nearly homogeneous field, plume growth may actually be somewhat slower than suggested by this formulation and may be satisfactorily computed using a constant diffusivity. Based on evidence from the behavior of sewage plumes in the early stages, a value on the order of 10^3 cm^2/second is indicated.

Horizontal dispersion in water bodies categorized as still water occurs by turbulent dispersion in the absence of any bulk horizontal movement of the receiving water body. If wind-driven or offshore currents are present, the still water assumption does not apply since the water velocity component must be incorporated in the governing partial differential equation. In this case, the concentration pattern is distorted by a projection along the direction of the wind velocity or prevailing water current. Where significant currents exist, the turbulent dispersion of the chemical in the current direction is usually neglected in comparison to the bulk transport of the dispersing chemical by the prevailing current.

b. Molecular Diffusion

With molecular diffusion, the spreading of a substance is driven by the existence of concentration gradients and the water is assumed to be isotropic so that the diffusion rates are equal in each direction. However, once an estimate of the diffusion coefficient, D^o_{AB}, is obtained, different multiples of this value can be applied to develop different estimates of the dispersion coefficients e_x, e_y, and e_z.

(1) Estimation Equation

The molecular diffusion coefficient of the spilled chemical in water is computed using the Wilke and Chang[34] method discussed by Reid and Sherwood[14], and the equation is written as:

$$D^o_{AB} = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \tag{361}$$

where,

D^o_{AB} = mutual molecular diffusion coefficient of solute A at very low concentrations (infinite dilution) in solvent B, in units of cm^2/second

M_B = molecular weight of solvent B (taken as 18.02 for water)

T = absolute temperature, °K

μ_B = viscosity of solvent B, centipoise

V_A = molal volume of solute A at its normal boiling temperature, $\text{cm}^3/\text{g mole}$

ϕ = dimensionless association factor of solvent B (taken as 2.6 for water)

Substituting the constants for water as the solvent gives the result:

$$D^o_{AB} = (7.4 \times 10^{-8}) \sqrt{(2.6)\ (18.02)}\ \frac{T}{\mu_B\ V_A^{0.6}}$$

$$D^o_{AB} = 5.06 \times 10^{-7}\ \frac{T}{\mu_B\ V_A^{0.6}} \tag{362}$$

The coefficient, D^o_{AB}, represents a *limiting diffusion coefficient at infinite* dilution of solute A in solvent B, and Reid and Sherwood discuss temperature, concentration, and other effects in subsequent sections. Other forms of the estimation equation are described, such as:

$$D^o_{12} = \frac{14.0 \times 10^{-5}}{\mu_B^{1.1}\ V_A^{0.6}} \tag{363}$$

which does not include a direct temperature term.

(2) Viscosity Computation

For use in the Wilke and Chang equation, viscosity of water as a function of temperature, at atmospheric pressure, may be obtained using an empirical equation referenced in the Chemical Engineers' Handbook[35]:

$$\frac{1}{\mu} = 2.1482 \left[(t - 8.435) + \sqrt{8078.4 + (t - 8.435)^2} \right] - 120 \qquad (364)$$

which is further referenced as having originally been obtained from Bingham ("Fluidity and Plasticity," p. 340, McGraw-Hill, New York, 1922).

Selected values for the viscosity of water in centipoise (cp) tabulated in the Chemical Engineers' Handbook, and listed as having been obtained from this equation include:

μ_w = 1.7921 cp @ t = 0°C
1.0050 cp @ t = 20°C
0.6560 cp @ t = 40°C
0.4688 cp @ t = 60°C
0.3565 cp @ t = 80°C
0.2838 cp @ t = 100°C

Although the viscosity values are tabulated in units of centipoise, a sample calculation using the equation with temperature in units of °C indicates that in the form written, the equation actually gives values of viscosity in units of poise. Since 1 poise = 100 centipoise, the form of this equation for use with the Wilke and Chang equation is:

$$\frac{1}{\mu_w} = 0.021482 \left[(t_w - 8.435) + \sqrt{8078.4 + (t_w - 8.435)^2} \right] - 1.20 \qquad (365)$$

where,

μ_w = viscosity of water in centipoise at temperature t_w

t_w = water temperature, in °C

Although viscosities of water can be obtained outside the temperature range 0 to 100°C, practical considerations indicate that the water temperature should probably be constrained to lie at least within this range, or an even narrower range, say 0 to 40°C (or 32 to 104°F).

It is noted that the data on which this empirical equation is based were not recently obtained (1922 or earlier), and, for example that the viscosity given at 20°C is 1.005 cp versus the standard subsequently adopted for water of 1.002 cp at 20°C. However, this equation has the advantage over other estimating methods[36] of being given in a single form over the range 0 to 100°C, the computation is relatively simple, and the accuracy is well within any limits implied by the uncertainties of a spill environment.

(3) Molar Volume (Mathias Equation)

From the Chemical Engineers' Handbook, Fifth Edition[37], the molar liquid volume, V_b, at the normal boiling point of the solute may be obtained from (page 3-229):

$$V_b = \frac{M}{\rho'_{1b}} = \frac{1}{\rho_{1b}} \tag{366}$$

if ρ_l at t_b is known, and where:

M = molecular weight

ρ'_{lb} = density of the solute at its normal boiling point (t_b), gm/cm^3

ρ_{lb} = molar density at boiling point, g mole/cm^3

V_b = molar liquid volume at boiling point t_b, cm^3/g mole

Perry[37] then gives the Mathias Equation from the Second Edition of Reid and Sherwood[15] as:

$$\rho_l + \rho_v = \rho_{lb}\ (2 - T_r)/(2 - T_{br}) \tag{367}$$

where ρ_l and ρ_v are liquid and vapor molar densities, respectively, and

ρ_{lb} = molar density at boiling point, g mole/cm^3

T_r = reduced temperature, °K

= T/T_c, where T = temperature, and T_c = critical temperature

T_{br} = T_b/T_c where T_b is the normal boiling point

Perry indicates an average error resulting from this equation of approximately 2 percent up to T near T_c.

For $\rho_v << \rho_l$, the equation reduces to:

$$\rho_1 = \rho_{1b} \frac{(2 - T_r)}{(2 - T_{br})} = \rho_{1b} \frac{(2T_c - T)}{(2T_c - T_b)} \tag{368}$$

and in this form can be used to estimate either ρ_1 or ρ_{1b} if the other quantity is known at T or T_b, respectively.

For use with the Wilke and Chang equation, the molar volume at the normal boiling point can be obtained as:

(a) If the density of the solute at the boiling point is known:

$$V_b = \frac{M}{\rho'_{1b}} , \quad \rho'_{1b} = \text{density at boiling point, in gm/cm}^3 \tag{369}$$

V_b in cm^3/g mole

M in gm/g mole

(b) If the density of the solute is known at a temperature t:

$$V_b = \frac{1}{\rho_{1b}} = \frac{1}{\rho_1} \frac{(2 - T_r)}{(2 - T_{br})} = \frac{M}{\rho'_1} \frac{(2 - T_r)}{(2 - T_{br})} \tag{370}$$

where,

ρ'_1 = density of solute at temperature t (°C), in gm/cm^3

t = water temperature in °C

If the density of the spilled chemical at the boiling point, but not at water temperature, is available, the molar volume used in the Wilke Chang equation should be taken simply as

$$V_b = \frac{M}{\rho'_{1b}} \tag{371}$$

and the Mathias equation need not be used unless it is necessary to provide for computations when the density at t_b is not known. If the molar volume is obtained directly from the density of the spilled chemical at its normal boiling point, then data for the critical temperature and boiling point of the solute are not required.

(4) Summary

Summarizing the preceding, the molecular diffusion coefficient of the spilled chemical in water, based on the Wilke and Chang, method is given by:

$$D^o_{AB} = 5.06 \times 10^{-7} \frac{M}{\mu_w V_A^{0.6}} \tag{372}$$

where T_W is the temperature (absolute, °K) of the receiving water body.

The viscosity of water obtained from Bingham's expression is:

$$\frac{1}{\mu_w} = 0.021482 \left[(T_W - 8.435) + \sqrt{8078.4 + (T_W - 8.435)^2} \right] - 1.20 \tag{373}$$

where T_W, the temperature of the receiving water body, is in units of °C.

Finally, assuming that the density of the liquid chemical at its normal boiling point is known, the molar volume is given simply as:

$$V_A = \frac{M}{\rho'_{1b}} \qquad (374)$$

To simplify the resulting computation, these equations are re-written slightly to give:

$$(V_A)_r = \frac{1}{V_A} = \frac{\rho'_{1b}}{M} \qquad (375)$$

$$T'_W = (T_W - 8.435) \qquad (376)$$

$$(\mu_w)_r = \frac{1}{\mu_w} = 0.021482 \left[T'_W + \sqrt{8078.4 + T'_W \cdot T'_W} \right] - 1.20 \qquad (377)$$

$$D^o_{AB} = (5.06 \times 10^{-7})\ (T_W + 273.2)\ (\mu_w)_r\ (V_A)_r^{0.6} \qquad (378)$$

where T_W is used consistently in units of °C.

In the above form, the computation of the molecular diffusion coefficient requires data for the temperature of the receiving water body, the molecular weight of the spilled substance, and its density at its normal boiling point. Since for a given scenario these are all constants, the diffusion coefficient is a derived constant needed to be computed only once for a particular set of spill conditions.

For the water dispersion model, the molecular diffusion coefficient computation is required only in the case of spills into still water, for use in estimating approximate values of turbulent dispersion coefficients in the absence of any other information. The additional data required for the diffusion coefficient computation are not otherwise required for use within the model.

The equations used are straightforward and should not, under normal operation, be susceptible to numerical problems. The diffusion coefficient will be a positive quantity for all positive values of $(\mu_w)_r$ and $(V_A)_r$, and for values of T_W greater than -273.2°C. $(V_A)_r$ is positive for all positive values of M and ρ'_{lb}, and the equation used for $(\mu_w)_r$ gives positive values over the temperature range 0°C to 100°C.

Adequate constraints then include:

$$\text{If } M \leq 0.0, \text{ use } M = M_{default}$$

$$\text{If } \rho_{lb} \leq 0.0, \text{ use } \rho_{lb} = (\rho_{lb})_{default}$$

Reasonable limits for the water temperature are probably 0°C to 40°C, although to allow for conceivable situations a somewhat broader range is suggested, say, -10°C to 50°C.

c. Amplification Factors

Molecular diffusion occurs at a much slower rate than turbulent dispersion, and thus the molecular diffusion coefficient D^o_{AB} obtained by the preceding calculation may be several orders of magnitude smaller than the values of the turbulent dispersion coefficients e_x, e_y, and e_z.

Preliminary work to calibrate the concentrations obtained using scaled values of the molecular diffusion coefficient to estimate turbulent dispersion suggest that scale factors on the order of 10^3 are indicated. Accordingly, the estimates obtained from molecular diffusion for the turbulent dispersion coefficients, in the absence of any other data, are given as:

$$e_x = 10^3 D^o_{AB}$$

$$e_y = 10^3 D^o_{AB}$$

$$e_z = 10^3 D^o_{AB} \tag{379}$$

Considering the nature of the turbulent dispersion occurring in stratified bodies of water (reviewed in a preceding section), the use of $e_x = e_y$ is appropriate. However, in the presence of significant density gradients, a smaller relative value may be more appropriate for the vertical dispersion coefficient e_z, and further calibration for individual spill situations may be desirable.

SECTION IV

MODELS FOR NON-TIDAL RIVERS

1. INTRODUCTION

Dispersion of a spilled chemical into a non-tidal river can be viewed as equivalent to dispersion in still water, subject to the influence of two additional factors: (1) the bulk fluid motion of the river current and (2) the constraints imposed by the banks and bottom of the river channel. Section I identifies the river system coordinates and channel geometry.

Considering only the influence of the river motion, the flow is assumed to be uniform across the cross-section of the river, in the direction of the positive x axis, and the velocity is given as u. The center of mass of the dispersing chemical is transported downstream by the bulk fluid motion, moving with a velocity u so that the distance moved in time t is given by ut. Relative to the center of mass of the spilled substance, the coordinates become stationary, and the dispersion behavior of the still water case applies. Thus for spills into large rivers, far from shore, at times close to the start of the spill, insight into the character of the concentration distribution can be obtained from the still water behavior, adding a component ut to downstream distances to account for the bulk flow.

About the center of mass of the spilled substance, the initial concentration distributions are Gaussian so that for times greater than zero, the concentrations decrease with distance from the center of mass but have some value at all distances. However, at very large distances, the concentrations are very small. Conservation of mass can be applied to define a region of the water body or volume centered about the center of mass of the spilled substance, within which some fixed fraction, for example, 95 percent, of the total dispersing mass is initially contained.

As the elapsed time from the start of the spill increases, the volume containing the dispersing chemical both moves downstream with a velocity u and grows in size. The growth continues until either a channel bank or the river bottom is encountered. Further growth in that direction is impeded, and the nature of the concentration distribution is modified. The model assumes that these boundaries are impenetrable; thus, the amount of substance contained in the portion of the volume that would have grown beyond the channel banks or bottom is reflected back into the river channel. The method of obtaining the additional contributions to the concentration in the river channel of the reflected amount of substance involves summing concentration distributions from additional virtual spill sources or images located outside the boundaries of the river channel.

The model for the dispersion of a spilled chemical into a non-tidal river is based on three-dimensional diffusion during the initial stages of spreading, and on one-dimensional diffusion for the later stages when the spreading has been confined by the river banks and bottom. The water body is assumed to be non-isotropic, and the model is formulated assuming constant, but different, turbulent dispersion coefficients in each of the principal directions. Methods of developing estimates for the values of the turbulent dispersion coefficients are described, and the model is formulated to accept user-provided input data if available. In the absence of user values, appropriate equations for automatically providing estimates of the turbulent dispersion coefficients are employed.

2. STAGES OF DISPERSION

The river channel banks and bottom act to confine the distribution of a spilled substance and give rise to different stages of dispersion. Initially, except for spills very near to a bank of the river, the dispersion is essentially unconfined and three dimensional spreading occurs. During this stage the dispersion is described by near-field models. The distribution of the spilled chemical mass increases until at some time after the start of the spill, the confining effect of the channel bottom or one or both banks becomes significant. Generally, the influence of these constraints will first cause the concentrations to become more or less uniformly distributed along one of the lateral directions, usually depth, and further spreading during this stage of transition acts to even the distribution across the remaining direction of the cross-section, usually width. At some later time, the spilled substance becomes more or less evenly distributed across the entire river cross-section. Models based on this assumption and formulated to estimate the further distribution of the spilled chemical in time and downstream distance, x, are referred to as far-field models. This section describes the bases for the formulations of the different types of models, and methods for establishing transition criteria between the near-field and far-field regimes.

Differences between models for the different stages of dispersion include the formulation of the governing partial differential equation, the assumptions made regarding chemical behavior, and the methods of solution. Generally, reducing the dimensions of the spreading also reduces the complexity of the concentration equations and simplifies the necessary computations. The assumptions made in each case and the methods of solution do not ensure continuity of concentrations from one stage to another. This is not, however, a significant disadvantage since differences in regions of transition should be considered as reflecting the appropriate assumptions for each stage. A forced matching would be artificial and tend to obscure the significance of solutions obtained for each stage.

Since the different stages of dispersion reflect the physical behavior of a dispersing chemical mass, models of the dispersion in each stage, if properly formulated, should tend to estimate concentration behavior similar to that of the next stage at large times or distances. Thus, concentrations obtained from a 3-D model, if boundary effects of the river channel are included, will become more or less uniformly distributed across the river cross section, exhibiting the type of behavior assumed for the one-dimensional case. Depending on the complexity of three- or two-dimensional models and required data, and the relative advantages or disadvantages of the assumptions and estimated accuracy of a one-dimensional model, a trade-off is involved in determining whether to investigate one-dimensional behavior separately if accurate three-dimensional formulations are employed. Generally, there are advantages, but a three-dimensional model can provide quantitative descriptions of one-dimensional spreading, so the incorporation of one-dimensional analyses does not add anything that is inherently absent in a three-dimensional analysis.

a. Three-Dimensional Behavior

When a chemical is spilled into a stream or river, its behavior depends on a number of factors. These include the physical and chemical properties of the chemical, the flow conditions in the river, and the location and nature of the release. If the area of the source of the spill is small in relation to the size of the river, the dispersion of the chemical will be in all directions. In this phase, the dispersion is three-dimensional, and concentrations are obtained from the following form of the three-dimensional partial differential diffusion equation:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = \frac{\partial}{\partial x}\left(e_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(e_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(e_z \frac{\partial c}{\partial z}\right) - kc \qquad (380)$$

where the bulk flow of the river body occurs in the x direction at a constant uniform velocity u, and e_x, e_y, e_z are the dispersion coefficients in each of the x, y, z coordinate directions.

The three-dimensional equation is used to describe the nature of the concentration distribution near the spill location; hence, solutions are referred to as near-field equations. The concentrations in this region are significantly dependent on the location of the spill, manner of release, and a range of other local effects. As the distance from the spill location increases, the concentrations obtained from the near-field equations tend to become evenly distributed over the cross-section of the river, and localized effects of the spill conditions are reduced.

Since the cross-sectional variations of concentration are significant during this early stage of spreading, descriptions of the shape of the river cross-section and the river velocity distribution across the cross-section are necessary. The current model approach assumes a rectangular channel cross-section of constant width and depth and a constant river velocity, uniform over the river cross-section.

b. Two-Dimensional Behavior

In most open channels, the depth is much less than the width so that at some time after the release, the substance is well mixed vertically without being completely mixed horizontally. In this case, the dispersion of the chemical is continuing in only two directions. The integral of the concentration over the depth of the river gives a product of an average concentration as a function of x, y, and t (but not z) and the river depth d. Substitution of this result in the three-dimensional diffusion equation leads to the following two-dimensional equation:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = \frac{1}{d} \frac{\partial}{\partial x} \left(e_x \, d \, \frac{\partial c}{\partial x} \right) + \frac{1}{d} \frac{\partial}{\partial y} \left(e_y \, d \, \frac{\partial c}{\partial y} \right) - kc \qquad (381)$$

where the concentration c is a function of x, y, t. A similar equation can be obtained for the concentration if the uniform distribution occurs first across the width, instead of the depth, of the channel; however, this situation usually does not apply for river channel configurations of practical interest.

The concentration distribution during this stage of spreading is still significantly affected by localized spill conditions, particularly the spill location (illustrated by a spill near a bank of a broad, shallow river). The influence of local effects continues to diminish, however, as the distance from the spill location increases.

Generally models of three-dimensional distributions necessarily treat boundary conditions at the river banks and bottom and thus can be used during this stage of dispersion as well. Also the transition to one-dimensional spreading provides a much greater simplification, and as a result, two dimensional models do not appear to have received extensive attention.

c. One-Dimensional Behavior

Over a longer period of time and at larger distances from the spill location, the chemical also becomes fully dispersed horizontally, and further dispersion continues only in the longitudinal, x, direction. The transition through the stage of two-dimensional spreading results in the dispersing mass becoming approximately uniformly distributed over the entire cross section of the river channel. The integral of the concentration over the cross-sectional area gives a product of the area, A, and the cross-sectional average concentration as a function of x and t (but not y or z). Substitution of this result in the three-dimensional diffusion equation leads to the following one-dimensional equation:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = \frac{1}{A} \frac{\partial}{\partial x} \left(e_x \, A \frac{\partial c}{\partial x} \right) - kc \qquad (382)$$

where the concentration c is a function of x and t, and gives the average concentration over the cross-section of the river channel. This one-dimensional equation is often referred to as the one-dimensional Fickian model because it is based on Fick's theory of diffusion.

For one-dimensional models, the turbulent dispersion coefficient e_x is replaced by an effective longitudinal dispersion coefficient E which represents not only the dispersion represented by e_x, but also the dispersion of the chemical due to the differential velocities and concentrations across the river channel. It can be seen that if the formulation of the effective longitudinal dispersion coefficient E is different than e_x, the concentration distributions will be different, giving rise to a discontinuity between concentrations computed by one-dimensional and three-dimensional models. Since the basic model assumptions differ, it is not necessarily advisable to artificially remove the discontinuity if three-dimensional and one-dimensional models are applied to the same spill scenario.

Since the distribution across the cross section occurs at longer distances from the spill location, the equations describing the concentration distribution are referred to as far-field models. During this stage, localized effects at the spill location have become substantially diminished; further one-dimensional distribution is essentially independent of the spill location relative to the river channel banks.

Focus on the one-dimensional region of spreading, whether by means of separate one-dimensional models or application of three-dimensional models at long range, is particularly justified when the resulting model has potential application in developing information useful for responses to accidental discharges. Model results would be more useful in this type of situation if sufficient time were available to obtain and utilize the results; therefore, it is most likely that these results would be applied during far-field stages of spreading.

(1) Fickian Model

The model developed from the one-dimensional diffusion equation gives concentration equations in the form of Gaussian distributions and is referred to as a Fickian model because of the form of the equation. This form of the model has been incorporated in the water dispersion model and is described in detail in a following section of this report. There have been recent developments in modelling approaches that suggest more accurate or appropriate techniques may be applicable; however, the Fickian model has an advantage in that it is readily used.

(2) Modified Fickian Model

When the distance from the release of a pollutant to the observation point is sufficiently long, then the dispersion has entered the "Taylor" period and the one-dimensional Fickian model can be used. However, the length of time preceding the Taylor period may be long. Nordin and Sabol[38] have shown that for a portion of the Mississippi River downstream from its union with the Missouri River, the length of time is on the order of 90 hours.

Cheng[39] showed that by modifying the one-dimensional Fickian model, a one-dimensional model can be used to predict dispersion before the dispersion has entered the Taylor period. Cheng and Liu[40] showed that even within the Taylor period, the Fickian model fails to accurately predict dispersion in three ways: first, the Fickian model shows the peak concentration of the pollutant to be inversely proportional to $\sqrt{t}$ when, in natural streams, the attenuation is much faster. Secondly, the Fickian model shows that the standard deviation is proportional to the square root of t, when, in fact, it has been shown that the exponent lies between 0.42 and 1.0. Finally, the Fickian model gives a Gaussian distribution of concentration versus time when data has showed that the distribution is more skewed than the Gaussian distribution describes. These differences have led to further developments in modeling dispersion in the one-dimensional stage.

An alternate approach to dispersion modeling was introduced by Taylor[41]. Taylor's method approaches the diffusion problem from a Lagrangian viewpoint, following the particles as they flow through the field. Since particle motion is random, any attempt to follow particle motion must be based on the statistical properties of random motion. Taylor's theory measures the radius of inertia, σ_x, of an initially concentrated cloud of fluid particles after their simultaneous dispersion from a common origin. The radius in the x direction is:

$$\sigma'_x(t) = 2\overline{u'}^2_x \int_0^t (t - \tau') \, R_L(\tau') \, d\tau' \qquad (383)$$

where $\overline{u'}^2_x$ is the mean of the squared fluctuation component of the velocity in the x direction and

$$R_L(\tau') = \frac{u'_x(t) \; u'_x(t + \tau)}{\overline{u'}^2} \qquad (384)$$

This approach leads to a modified description of one dimensional behavior, obtaining concentrations using a Pearson-type-III distribution. A preliminary analysis for this type of model has been formulated, but further description has not been included in this report since several refinements are required to permit practical use.

d. Determination of Transition

During the initial stages of an instantaneous release, the dispersion of a spilled chemical is relatively unaffected by the presence of confining channel banks and bottom. With the form of the Gaussian solutions, the amount of substance contained within any distance from the center of mass of the spilled chemical is determined by the standard deviation of the distribution. Demarcation of zones of transition between the different stages of dispersion is based on the elapsed times at which significant or observable concentrations occur at a boundary surface, and these times are obtained from the standard deviations of the Gaussian distribution.

Considering a spill location on the surface of a river of half-width b and depth d, at an offset, a, from the centerline of the river, the distances from the spill location to each boundary are:

Distance to bank $(y = +b) = b - a$

Distance to bank $(y = -b) = b + a$

Distance to bottom $= d$

In the initial stages of dispersion, spreading occurs until the concentrations near one boundary become observable. Based on the distribution of mass about the center of a Gaussian distribution, this condition can be expressed in terms of a multiple of the standard deviation, considering the dispersing chemical to be contained within an expanding ellipsoid having the lengths of the semi-axes as σ_x, σ_y, and σ_z. From Section II, paragraph 3.a.(4), it was shown that for a one-dimensional distribution, 68 percent of the total mass is contained within a distance of σ about the center of the dispersing chemical, and 95 percent is contained within a distance of 2σ. Since $\sigma = \sqrt{2\,et}$, the time a particular distance is reached is readily obtained and related to the total quantity of mass dispersing from the spill site.

Letting the multiple of the standard deviation be written as n, the first channel constraint is reached at the earliest time given by:

$$(b - a)^2 = n^2 \sigma_y^2 = 2 n^2 e_y t$$

$$(b + a)^2 = n^2 \sigma_y^2 = 2 n^2 e_y t$$

$$d^2 = n^2 \sigma_z^2 = 2 n^2 e_y t \qquad (385)$$

The earliest time obtained for lateral dispersion will be given corresponding to the bank closest to the spill location. These times are dependent on the dispersion coefficients e_y and e_z, and the dimension of the river channel b = w/2 and z. In most surface water bodies the horizontal spreading (e_y) will be much faster than the vertical dispersion (e_z); however, most rivers of practical interest are much wider than deep.

For times greater than the smallest of the above, the effects of the first confining boundary becomes significant and the dispersion no longer occurs unconstrained in three directions. As further spreading occurs, the distribution grows until a second and a third channel boundary are reached. The time this occurs can be taken in proportion to the largest of the above values, although a substantial degree of mixing across the cross-section will actually be achieved earlier as a result of reflections from boundary surfaces. Beyond this time, further distribution can be considered a function of longitudinal distance x, and the far-field equations can be used.

This gives the maximum time for which unconfined dispersion occurs as the minimum of:

$$\frac{(|b| - |a|)^2}{2 n^2 e_y} \quad \text{and} \quad \frac{d^2}{2 n^2 e_z} \tag{386}$$

and the minimum time at which the uniform conditions appropriate to the far-field model are reached as the maximum of:

$$\frac{(|b| + |a|)^2}{2 n^2 e_y} \quad \text{and} \quad \frac{d^2}{2 n^2 e_z} \tag{387}$$

For values of n between 1 and 2, the coefficient $\frac{1}{2 n^2}$ lies between 0.125 and 0.50. A value of 0.3 has been assumed; however, lower values corresponding to n = 1 could be used to restrict the time over which unconfined three-dimensional spreading occurs and higher values corresponding to n = 2 for the well-mixed condition. The water body will not be thoroughly mixed until the longest of these times, at which stage a one-dimensional model can be applied. A three dimensional model could continue to be used if terms for boundary conditions are included. Since the river spills are assumed to occur at a location, a, offset from the river centerline, the minimum time obtained above could be virtually the time of spill; to adequately model the initial stages for such a spill, it is necessary to include the boundary terms in the three-dimensional equations and to set the transition to a one-dimensional equation using a maximum time.

When information about the relative location of the spill is not known or unavailable, the distances in the above equations are taken to be proportional to the characteristic dimensions of the water body. Further methods to determine the appropriate constants of proportionality for the time at which one-dimensional behavior may be assumed are described in the following paragraphs.

The equation used to calculate the distance from the source of the release at which one can begin to use 1-D models was first presented by H.B. Fischer in 1967[42]. Fischer measured the length of the convective period, the period in which the two-dimensional equation describes the dispersion, in order to determine the length of time that must pass after the release of the substance before the Fickian model can be used.

The time scale which was used to measure the convective period was derived by estimating the time required for cross-sectional mixing T_E (the Eulerian time scale) and by evaluating the Lagrangian time scale, T_L'. Using dimensional analysis of cross-sectional mixing, he found that,

$$T_E = \frac{\ell^2}{e} \tag{388}$$

where e is a mixing coefficient for the section and ℓ is a characteristic length. For two-dimensional flow, the average value of the vertical mixing coefficient, based on the distribution of shear and the Reynolds analogy, is

$$\bar{e}_z = \frac{kdU_*}{6} \qquad (389)$$

where k = von Karman constant

d = characteristic depth

U_* = shear velocity

Substitution gives the equation for T_E in the approximate form:

$$T_E = \frac{6d}{kU_*} \qquad (390)$$

Fischer further found that the Lagrangian time scale:

$$T_L' = \frac{0.404d}{kU_*} \qquad (391)$$

Putting T_L' in terms of T_E yielded:

$$T_E = 14.8T_L' \qquad (392)$$

In natural streams, lateral mixing is the most important factor within the Eulerian time scale. Elder[43] presented an equation for lateral mixing for two-dimensional flow where e_y is the lateral mixing coefficient:

$$e_y = \alpha \, d \, U_* \qquad (393)$$

where $\alpha = 0.23$.

Substituting into the expression for T_E gives:

$$T_E = \frac{\ell^2}{0.23 \, R_h \, U_*} \qquad (394)$$

where d is replaced by the hydraulic radius, R_h.

The Lagrangian time scale for two-dimensional flows in natural streams can now be calculated as:

$$T_L' = \frac{0.30 \, \ell^2}{R_h \, U_*} \qquad (395)$$

Most recent research has found that Elder's value for α is too low. A more precise value would be 0.84. This value was given by Cheng[39] in a paper in which the values of α were given for five rivers. The range of values was from 0.357 to 2.0 with the average being 0.84.

It is well known that the value of α is dependent upon the curvature of the river. Several investigators (Yotsukura, et al, [4] Sayre and Yeh[45]) have found that values for α range from 0.6 in the curving reach of the Mississippi River to 10.0 for a sharp bend. Both Fischer[46] and Yotsukura and Sayre[47] have suggested equations to predict the value of e_y for the river curvature. However, as Yotsukura and Sayre[47] point out, the results from present equations are, as yet, imprecise.

To measure the length of the convective period, the period before which the 1-D model can be successfully used, Fischer[42] used the dimensionless time factor $t' = \frac{t}{T'_L}$. In order to identify the end of the convective period, three criteria were used. First, the concentration distribution over any cross section must approach the steady-state profile. Secondly, the variance should grow linearly, and thirdly, the concentration should decay as predicted by the diffusion equation. These three criteria were satisfied when $t > 6$. If the onset of the 1-D phase is at six times the Lagrangian time scale, by changing from a time measurement to a length measurement, the distance from the source of the release to the point where a 1-D model can be used is:

$$L > \frac{1.8\ \ell^2\ U}{R_h\ U_*} \tag{396}$$

3. NEAR-FIELD INSTANTANEOUS SPILL MODEL

The general form of the solutions to the diffusion equation in three dimensions is obtained as a product of three one-dimensional distributions, to describe the concentration distribution relative to the center of mass of the spilled chemical. For a spill into a moving river, having a bulk fluid velocity, u, in the longitudinal direction, x, the center of mass of the spilled chemical is translated a distance ut in time t so that the longitudinal coordinate relative to the center of mass becomes $x - ut$, where x is measured from the spill origin.

a. General Solution

Applying this transformation to the distribution along x, the three-dimensional product of distributions for an instantaneous point source is obtained as:

$$c(x,y,z,t) = A \cdot \frac{1}{\sigma_x} e^{-\frac{(x-ut)^2}{2\sigma_x^2}} \cdot \frac{1}{\sigma_y} e^{-\frac{y^2}{2\sigma_y^2}} \cdot \frac{1}{\sigma_z} e^{-\frac{z^2}{2\sigma_z^2}} \qquad (397)$$

where A is a constant to be determined from conservation of mass, and the standard deviations are:

$$\sigma_x = \sqrt{2 e_x t}$$

$$\sigma_y = \sqrt{2 e_y t}$$

$$\sigma_z = \sqrt{2 e_z t} \qquad (398)$$

The dispersion coefficients e_x, e_y, and e_z will, in general, have different values in each direction.

The form of the concentration distribution given above applies for an instantaneous point source, in the absence of decay (k=0). Solutions for non-conservative substances (k>0) are obtained by the inclusion of the term e^{-kt} as an additional product. It can be verified by substitution that this form of the concentration distribution satisfies the three-dimensional partial differential equation applicable for this type of water body (u>0, v = w = 0) given in Section IV, paragraph 2.a. Also, the form of the concentration equation itself reduces to the still water equation as the bulk transport velocity u becomes small. However, the dispersion coefficients are computed as functions of u, so the model does not identically reduce to the still water case.

Conservation of mass requires that, in the absence of any sinks or sources, the total mass of a conservative substance dispersing in the environment at any time t be equal to the total mass of substance, M, orginally released instantaneously at the spill location (x=0). The total mass is obtained as the integral of the concentration over the volume of the receiving water body. Since the river model provides for dispersion constrained by the river channel, a method of superposition or imaging is used to construct solutions for constrained flow from unconstrained distributions.

For unconstrained dispersion, the spill is assumed to occur on the surface of the water body, and the z coordinate (depth) extends from the surface (z=0) to an infinite depth. The lateral dimension y is initially assumed to vary from 0 in each direction (an offset of the spill location from the river centerline is introduced later but does not affect this analysis). The mass integral is expressed about the center of the spilled chemical mass, using the longitudinal coordinate transformation $x_m = x - ut$. This gives for the mass contained within a rectangular volume of length 2 x_m and width 2y, centered about the center of the moving chemical mass, and depth z below the surface:

$$M(x_m,y,z,t) = \frac{A}{\sigma_x \sigma_y \sigma_z} \int_0^z \int_{-y}^{y} \int_{-x_m}^{x_m} e^{-\frac{x_m^2}{2\sigma_x^2}} e^{-\frac{y^2}{2\sigma_y^2}} e^{-\frac{z^2}{2\sigma_z^2}} \, d\, x_m \, dy \, dz \qquad (399)$$

Since the coordinate transformation from x to x_m yields an equation for the mass distribution that is identical to the still water case, the mass distribution is obtained directly from Section III, paragraph 2, substituting $x_m = x - ut$, as:

$$M(x,y,z,t) = \frac{A\ (2\pi)^{3/2}}{2}\ \mathrm{erf}\left(\frac{(x - ut)}{\sigma_x\sqrt{2}}\right)\ \mathrm{erf}\left(\frac{y}{\sigma_y\sqrt{2}}\right)\ \mathrm{erf}\left(\frac{z}{\sigma_z\sqrt{2}}\right) \qquad (400)$$

which gives a general expression for the total mass contained in a volume $z \cdot 2y \cdot 2\ (x - ut)$ as a function of time; the volume moves downstream at a velocity u, so the distance x in this equation is constrained: $x > ut$.

As the dimensions of the volume are taken to be increasingly larger, the error function values approach the limit of 1, giving for the total mass in the system:

$$M = \lim_{\substack{x\to\infty \\ y\to\infty \\ z\to\infty}} M(x,y,z,t) = \frac{A}{2}\ (2\pi)^{3/2} \qquad (401)$$

where M is the amount of chemical initially introduced instantaneously at the spill location. The limit value reached for M(x,y,z,t) is not a function of time (a conservative chemical was assumed for simplicity), satisfying conservation of mass. The constant coefficient A is now obtained in terms of the spill quantity M as:

$$A = \frac{2\ M}{(2\pi)^{3/2}} \qquad (402)$$

Substituting this result, incorporating the decay term, and expressing the standard deviations in terms of the dispersion coefficients, gives the general form of the concentration equation for an instantaneous release in a non-tidal river as:

$$c(x,y,z,t) = \frac{M}{4\ (\pi)^{3/2}\sqrt{e_x\ e_y\ e_z}\ t^{3/2}}\ e^{-\frac{(x-ut)^2}{4\ e_x t}}\ e^{-\frac{y^2}{4\ e_y t}}\ e^{-\frac{z^2}{4\ e_z t}}\ e^{-kt} \qquad (403)$$

This equation expresses concentrations in a contaminant zone, identified as containing concentrations in excess of a hazard level, which moves downstream at the current velocity u, increases in size until the maximum extent of spreading of the hazard level is reached, and then, while still moving downstream, decreases in size until the zone collapses back to a point. The equation describes a point source behavior, and it can be seen that the term $t^{3/2}$ in the denominator will produce infinite initial concentrations at the spill origin.

The concentration equation above applies to unconfined dispersion for a spill located on the surface at the centerline of the water body. Before the equation can be applied, the effect of the spill location offset and the channel constraints need to be incorporated.

b. Boundary Conditions

Section I, paragraph 4, describes the river system coordinates and channel geometry. The concentration equations obtained for unconfined flow describe concentration distributions relative to the center of mass of the spilled substance, and Section I, paragraph 4.(1), describes the transformations between spill coordinates (α,β,γ) and water body coordinates (x,y,z).

For spills into non-tidal rivers, at the surface (x=0, z=0) at a point in the channel offset from the centerline by a distance given as a (positive a corresponding to an offset in the positive y direction), two transformations are required:

$$\alpha = x - ut$$

$$\beta = y - a$$

$$\gamma = z \tag{404}$$

These give the concentration equation in the form:

$$c(x,y,z,t) = \frac{M}{4\,(\pi)^{3/2}\sqrt{e_x\,e_y\,e_z}\;t^{3/2}}\,e^{-\frac{(x-ut)^2}{4\,e_x t}}\;e^{-\frac{(y-a)^2}{4\,e_y t}}\;e^{-\frac{z^2}{4\,e_z t}}\;e^{-kt} \tag{405}$$

Since conservation of mass was applied to this form of the equation, the concentrations obtained apply to all values of the coordinates (α,β) or (x,y) and values of γ and z greater than zero, that is, dispersion unconfined by channel banks and bottom. This implies unlimited permeability of the banks and bottom to the pollutant in the river. The treatment of adsorption and penetration is most complex, and the nature of the variations and interactions of chemical behavior and channel conditions cannot be reasonably incorporated in a generalized model of this type. Thus, a simplifying assumption is made that no dispersion of the pollutant occurs through the banks or bottom of the river. Generally, this assumption tends to be conservative leading to higher estimates of concentrations in water than might actually occur. Also, later release or dissolution of adsorbed pollutant may contribute to longer durations of residual concentrations than estimated by the model.

The boundary conditions to be applied then are such that no transfer of the pollutant occurs across the river surface (z=0) or through the channel banks (y = ±b) and bottom (z=d). Since conservation of mass has been applied, the (initial) boundary condition at the surface is satisfied. For simplicity in the following derivation, the concentration equation is summarized using abbreviated notation as:

$$c(x,y,z,t) = f(x)\ g(y)\ h(z) \tag{406}$$

where

$$f(x) = \frac{M}{4\ (\pi)^{3/2} \sqrt{e_x\ e_y\ e_z}\ t^{3/2}}\ e^{-\frac{(x-ut)^2}{4\ e_x t}}\ e^{-kt} \tag{407}$$

$$g(y) = e^{-\frac{y^2}{4\ e_y t}} \tag{408}$$

$$h(z) = e^{-\frac{z^2}{4\ e_z t}} \tag{409}$$

Only the dependence on the spatial coordinates is retained in the notations for f(x), g(y) and h(z) since this is required for the adjustment to satisfy the boundary conditions.

For the spill located at an offset, a, from the center of the river channel, the function g is initially taken as g(y-a). At times t > 0, the concentration distribution in each direction is Gaussian, and concentration values will exist at long distances from the spill location. These will increase in time to a maximum and then decrease. In particular, the Gaussian distribution will give non-zero concentrations beyond the channel banks and bottom so that conservation of mass within the river channel will not be maintained. Considering first the channel bottom at $z=d$, the concentrations on the bottom, at any time t, are obtained as:

$$c(x,y,d,t) = f(x)\ g(y-a)\ h(d) \tag{410}$$

The boundary condition of no transfer across the channel bottom is obtained by providing a second or image spill source located at a distance d symmetrically below the channel bottom to produce concentrations at the bottom surface of equal magnitude to those produced by the primary spill source. Spill coordinates relative to the location of this first image source are given by

$$\alpha = x$$

$$\beta = y - a$$

$$\gamma = z - 2d \tag{411}$$

and the concentrations in the river channel are summed to give:

$$c(x,y,z,t) = f(x)\ g(y-a)\ h(z) + f(x)\ g(y-a)\ h(z-2d) \tag{412}$$

As a new source, however, the image at $\alpha = x$, $\beta = y-a$, $\gamma = z-2d$ produces concentrations at the surface of $f(x)\ g(y-a)\ h(-2d)$, and a second image source, located above the surface, is required to maintain the boundary condition of no transfer across the surface. This second image, located at an equal distance above the surface as the first image is below it, that is, at $z = +2d$, produces concentrations to reflect the distribution from the first image about the surface and the resulting concentrations in the river channel are summed to give:

$$c(x,y,z,t) = f(x)\ g(y-a)\ h(z) + f(x)\ g(y-a)\ h(z-2d)$$

$$+ f(x)\ g(y-a)\ h(z+2d) \tag{413}$$

Since the second image now produces concentrations at the channel bottom of $f(x)\ g(y-a)\ h(3d)$, this process can be repeated indefinitely, locating image sources alternately below the bottom and above the surface at coordinates $z = +2d, -2d, +4d, -4d, +6d, -6d$, and so forth to give

$$c(x,y,z,t) = f(x)\ g(y-a)\left\{ h(z) + \sum_{n=1}^{\infty}\left[h\ (z-2nd) + h(z+2nd)\right]\right\} \tag{414}$$

However, as the distance from the origin increases, the contribution of each additional image source to the concentration of the pollutant in the river channel becomes increasingly small and, for a first order approximation, only the first two image sources are retained to give:

$$c(x,y,z,t) = f(x)\ g(y-a)\left[h(z) + h(z-2d) + h(z+2d)\right] \tag{415}$$

Next, the spill at (0,a,0) and each of the image sources at (0,a,2d) and (0,a,-2d) contribute to concentrations at the river channel banks, y = ±b, and the boundary conditions at the banks are satisfied by locating additional image sources to reflect the concentrations about each bank. First, for the primary source, the boundary condition at the left bank (y = +b) is maintained by locating an image at an equal distance on the opposite side of the bank or at y = 2b-a. The boundary condition at the right bank (y = -b) is maintained by locating an image at an equal distance from the primary source, but on the opposite side of the bank at y = -2b-a. Since each of these new image sources will disturb the boundary conditions at the opposite banks, additional images can be indefinitely located, for repeated reflections about each bank, at coordinate locations y = -4b+a, 4b+a, -6b-a, 6b-a, and so forth. As before, considering only a first order approximation requires images located at y = 2b-a and y = -2b-a, for each source and image at z = 0, z = +2d and z = -2d so that summing the contributions from the source and each first order image gives for the concentration in the channel:

$$c(x,y,z,t) = f(x) \cdot \left[g(y-a) + g(y-2b+a) + g(y+2b+a)\right]$$

$$\cdot \left[h(z) + h(z-2d) + h(z+2d)\right] \qquad (416)$$

If the spill source is located in the center of the channel at a = 0, the image sources become symmetrically distributed at y = +2b, -2b. As the value of a approaches either bank at ±b, the distance between the source location and the image reflected about that bank approaches 0, and therefore the distance between the reflection of both this image and the source about the opposite bank approaches zero. Thus, for these limit cases ($a = \pm b$), the accuracy of the first order approximation is somewhat diminished since there will be one second order term having the same value as the smallest first order term. For insight into the conditions under which higher order image terms may be neglected, further discussion is given in reference[20].

At the channel banks and bottoms, the reflection of the dispersing chemical by the image sources will distort the movement of the dispersing chemical, and, after the initial stages of unconfined dispersion, depending on the cross-channel position of the spill origin, the location of maximum concentration may shift away from the original position of the center of the moving spill mass. Also for spills at an offset $a > 0$, it can be seen that the concentration distribution does not remain symmetrical in the cross-section about the axis $y = a$.

c. Model Equation

Incorporating the image source terms and substituting for the abbreviated notation give the form of the concentration equation for instantaneous point source spills into non-tidal rivers as:

$$c(x,y,z,t) = \frac{M}{4\,(\pi)^{3/2}\sqrt{e_x\,e_y\,e_z}\;t^{3/2}}\; e^{-\frac{(x-ut)^2}{4\,e_x t}}\; e^{-kt}$$

$$\cdot \left[e^{-\frac{(y-a)^2}{4\,e_y t}} + e^{-\frac{(y-2b+a)^2}{4\,e_y t}} + e^{-\frac{(y+2b+a)^2}{4\,e_y t}} \right]$$

$$\cdot \left[e^{-\frac{z^2}{4\,e_z t}} + e^{-\frac{(z-2d)^2}{4\,e_z t}} + e^{-\frac{(z+2d)^2}{4\,e_z t}} \right] \qquad (417)$$

where M is the mass of pollutant released, x, y, z are the downstream, cross stream, and vertical depth coordinates, t is elapsed time from the start of the spill, u is the mean stream velocity, 2b=w the mean width of the stream, d the depth, a represents the location of the spill point on the surface, e_x, e_y, and e_z are the respective turbulent dispersion coefficients, and k is the decay coefficient representing the degradation of chemical due to chemical reaction or biological assimilation. Since in this form the boundary conditions at the surface, channel banks, and bottom are generally approximately satisfied, the equation applies, to within the first order approximation, for all values of x, y, z and could be used even for large values of x instead of assuming a uniform cross-sectional distribution.

d. Determination of Dispersion Coefficients e_x, e_y, e_z

Turbulent dispersion in rivers depends on river geometry and flow rates, and equations for the dispersion coefficients previously obtained [12] are given by:

Dispersion Coefficients	Very Wide Rivers (w/d > 100)	For Narrow Rivers (w/d < 100)
e_z	$0.067\ U^* R_h \sim 0.067\ U^* d$	$0.067\ U^* R_h$
e_x	$0.1\ e_z$	$0.1\ e_z$
e_y	$0.1\ e_z$	$0.23\ U^* R_h$

where

d = mean depth of flow, meters

w = mean river width, meters

R_h = hydraulic radius, meters

U^* = shear velocity, meters/second

e_x, e_y, e_z = turbulent dispersion coefficients, meters^2/second

The width-to-depth ratio $w/d \sim 100$ is assumed to be the upper limit for the side banks of the river to have any influence on the transverse velocity distribution. However, Holley et al[48] have used $w/d \sim 600$ for estuaries in the tidal regions. For the vertical dispersion coefficient, if the width-to-depth ratio is large, the hydraulic radius is approximately equal to the river depth; this simplification is indicated but not required for computation.

Recent investigations appear to suggest that the transverse dispersion coefficient e_y may be significantly underestimated by these equations, and for wide rivers e_y should be larger with respect to e_z than presented.

(1) Effect of River Curvature

Elder[43] presented an equation for lateral mixing for two-dimensional flow where e_y is the lateral mixing coefficient:

$$e_y = \alpha \, d \, U_* \qquad (418)$$

where the coefficient α was given as 0.23. Most recent research has found that Elder's value for α is too low. A more precise value would be 0.84. This value was given by Cheng[39] in a paper in which the values of α were given for five rivers. The range of values was from 0.357 to 2.0 with the average being 0.84.

It is well known that the value of α is dependent upon the curvature of the river. Several investigators (Yotsukura, et al,[44] Sayre and Yeh [45]) have found that values for α range from 0.6 in the curving reach of the Mississippi River to 10.0 for a sharp bend. Both Fischer[46] and Yotsukura and Sayre[47] have suggested equations to predict the value of e_y for the river curvature. However, as Yotsukura and Sayre[47] point out, the results from present equations are, as yet, imprecise, and empirical methods to obtain appropriate values of α are not available.

As a result, the dispersion coefficient e_y is assumed to be obtained using a value of $\alpha = 0.84$, and this should be a reasonably good estimate of an average coefficient over a region of several bends. However, the value of α will increase within a bend of a river. For spills into a curved river channel, values of α on the order of 3.0 could be more appropriate for use in the near-field equations. Values of α of about 0.3 would apply for spills into relatively straight channels.

The distribution of mass from an instantaneous spill is modeled by Gaussian functions where the distance covered by the dispersing mass is proportional to the standard deviation $\sigma = \sqrt{2\ et}$. Thus, larger values of the coefficient α will contribute to a faster rate of dispersion and hence more quickly reduce the concentrations. Use of smaller values of α, appropriate for straight channels, will therefore tend to give conservative results.

(2) Reformulation of Equations

Based on the above, the expression for e_y is revised, and it appears that a distinction between narrow and wide rivers is no longer appropriate. Retaining the coefficient, α, the equations for the turbulent dispersion coefficients are written as:

$$e_z = 0.067\ U^* R_h \tag{419}$$

$$e_x = 0.1\ e_z \tag{420}$$

$$e_y = \alpha\ U^* R_h \tag{421}$$

where a nominal value of 0.84 is assumed for α.

(a) Hydraulic Radius

The hydraulic radius, R_h, appearing in the computation of the turbulent dispersion coefficients is defined as the cross-sectional flow area of a river divided by the wetted perimeter and has the dimensions of length.

For w = river width, and

d = river depth

the hydraulic radius is given by:

$$R_h = \frac{\text{cross-sectional area} = w \cdot d}{\text{wetted perimeter} = d + w + d} \tag{422}$$

and this can be written as:

$$R_h = d \cdot \frac{w/d}{2 + w/d} = w \cdot \frac{1}{2 + w/d} \tag{423}$$

From this, it can be seen that for very wide rivers, as in the case of $w/d > 100$, the definition of the hydraulic radius gives $R_h \sim d$, and for very narrow rivers where w/d is small, $R_h \sim w/2$. Approximate values of the coefficient in the expression for the hydraulic radius are tabulated below for a range of width-to-depth ratios selected to illustrate these limit conditions:

Width-to-Depth Ratio, w/d	Hydraulic Radius, R_h
0.001	$R_h = 0.0005\ d = 0.50\ w$
0.01	$R_h = 0.005\ d = 0.50\ w$
0.10	$R_h = 0.048\ d = 0.48\ w$
1.00	$R_h = 0.33\ d = 0.33\ w$
10.0	$R_h = 0.83\ d = 0.083\ w$
100.0	$R_h = 0.98\ d = 0.0098\ w$
1000.0	$R_h = 0.998\ d = 0.001\ w$

(b) Shear Velocity

The shear velocity, U^*, is given by:

$$U^* = \sqrt{\tau_o/\rho} = 3.115\ n\ u/R_h^{1/6},\ \mathrm{m/s} \tag{424}$$

where

τ_o = wall shear stress,

ρ = density of fluid,

n = manning roughness factor, and

u = average velocity of cross section

(c) Manning Roughness Factor

The Manning formula relates the mean velocity to the hydraulic gradient:

$$u = \frac{1.486}{n} R_h^{2/3} s^{1/2} = \frac{1.486}{n} R_h^{1/6} \sqrt{R_h s} \qquad (425)$$

where

u = mean velocity

R_h = hydraulic radius

s = hydraulic gradient

n = coefficient of roughness

In typical use, u is in units of feet per second, R_h in feet.

For natural stream channels, values of the Manning factor are:

0.020	Smooth earth or firm gravel
0.030	Clean, straight bank, full stage, some stones and weeds
0.040	Winding, some pools, and shoals

0.055	Winding, some pools, shoals and stony sections
0.070 - 0.125	Sluggish reaches, very deep pools, very weedy or obstructed with debris

(3) Computational Use

The preceding equations give the dispersion coefficients in units of m^2/second, and for use in computations in CGS units, conversion of the coefficient values is required.

The turbulent dispersion coefficients (e_x, e_y, and e_z) are computed as functions of the spill scenario data items d, w, u, and n. Thus, these coefficients are themselves constant for any particular assessment run and need only be calculated once at the start of a run. Thereafter, the coefficients can be treated as if they were, in fact, data items entered by the user.

If both d and w are zero, the expression for the hydraulic radius will fail. Also, the result obtained for e_z will be unpredictable if either or both are negative. Since neither situation is realistic, a constraint should be included such that

$$\text{if } w \leq 0.0,\ w = w_{default}$$

$$\text{if } d \leq 0.0,\ d = d_{default}$$

The coefficient e_z will be zero if u or n are zero. Since these are physical quantities, a constraint is required to prevent negative values. This dependence of the dispersion coefficients on the river velocity u limits the application of the model to moving water bodies. If values of the dispersion coefficients are obtained independently of this computation, then the river model with the adjusted dispersion coefficients could be used to model lake or ocean behavior with $u = 0$. Taking the distance to the river banks as very large, the channel bottom can be used to model the effects of stratification in lakes or the ocean.

The Manning roughness factor must also be greater than zero.

4. FAR-FIELD INSTANTANEOUS SPILL MODEL

According to the criteria established in Section IV, paragraph 2.c, at distances sufficiently far from the spill location, the discharging chemical can be considered to have become uniformly distributed across the cross-section of the river channel. Further dispersion takes place longitudinally and is described by a one-dimensional model. The form of the governing partial differential diffusion equation, for constant river cross-section and longitudinal dispersion coefficient, becomes:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = E \frac{\partial^2 c}{\partial x^2} - kc \qquad (426)$$

where c is the cross-sectional average concentration as a function of distance from the spill location x, and elapsed time from the start of the spill, t. The characteristics of the solution to the one-dimensional diffusion equation are extensively described in Section II of this report.

a. General Solution

Referring to Section II, the general form of the solution to this equation can be written directly as:

$$c(x,t) = \frac{a}{\sqrt{Et}} e^{-\frac{(x-ut)^2}{4Et}} e^{-kt} \qquad (427)$$

where a is a constant to be determined from conservation of mass and E is the longitudinal dispersion coefficient. It can be verified by substitution that this form of the concentration equation satisfies the diffusion equation.

Conservation of mass requires that the integral of the concentration over the volume of the water body is equal to the total quantity of substance in the environment. Because both the concentration and the total mass are related in the same manner to the exponential decay term (k), this factor can be ignored and conservation of mass stated more simply in terms of a conservative pollutant: the total mass dispersing in the water body at any time t is equal to the total mass initially spilled, M. This gives the equation:

$$M = \iiint c(x,t)\,dx\,dy\,dz = \int_{-\infty}^{\infty} c(x,t)\,dx \cdot \iint dy\,dz \qquad (428)$$

The integral over the dimensions of the water body in the y and z directions is simply the cross-sectional area of the river channel and is denoted by A. Substituting the form of the concentration equation then gives:

$$M = A \int_{-\infty}^{\infty} \frac{a}{\sqrt{Et}}\, e^{-\frac{(x-ut)^2}{4Et}}\,dx \qquad (429)$$

where the exponential decay term is ignored. The integral is evaluated using the definition of the error function to obtain:

$$M = 2\ a\ A \int_{-\infty}^{\infty} e^{-\xi^2}\ d\xi = 2\ a\ A \cdot \sqrt{\pi} \tag{430}$$

Solving for the constant a gives:

$$a = \frac{M}{2\ A\sqrt{\pi}} \tag{431}$$

Finally, substituting the value of the constant a in the general equation for c(x,t) gives the result:

$$c(x,t) = \frac{M}{2\ A\sqrt{\pi}\sqrt{Et}}\ e^{-\frac{(x-ut)^2}{4Et}}\ e^{-kt} \tag{432}$$

This solution applies for all values of x, $-\infty < x < \infty$, and for $t > 0$. It can be seen that for large values of x or t, the concentration approaches a limit value of zero.

b. Determination of Longitudinal Dispersion Coefficient

Over the past quarter century, many empirical equations have been suggested by various investigators to predict the value of the longitudinal dispersion coefficient. The following review focuses on those most pertinent equations that either have influenced future investigators or have been shown to estimate values to within a small order of magnitude from observed data.

Taylor[41], as the earliest investigator, showed that for flow in a long, straight circular pipe, the value of the longitudinal dispersion coefficient, E, is:

$$E = 10.11\ U^{*}\ r \tag{433}$$

where U^{*} is the shear velocity and r is the radius of the pipe.

Elder's[43] investigation in 1959 showed that for open channels:

$$E = \alpha\ U^{*}\ d \tag{434}$$

where α has the value 5.93 and d is the depth of flow. Various investigators, such as Krenkel[49], and Yotsukura and Fiering[50] found different values for α; the former finding $\alpha = 9.1$ and the latter showing $\alpha = 13.0$.

Reference[12] utilized Elder's equation, noting that for wide rivers, $w/d > 100$, the hydraulic radius is approximately equal to the depth, to obtain

$$E = \beta\ n\ u\ R_h^{5/6} \tag{435}$$

where $U^{*} = 3.115\ n\ u/R_h^{1/6}$, and

$$d \approx R_h \tag{436}$$

A value of $\beta = 63$ was used with MKS units to obtain E in m^2/second.

For narrow rivers, $w/d < 100$, reference[12] expressed the form of the longitudinal dispersion coefficient from Elder's equation using the characteristics of the velocity distribution as:

$$E = 0.3 \frac{u''}{U^*} \frac{b^2}{R_h} \tag{437}$$

but suggested that in this range a nearly constant relationship between $\frac{E}{R_h U^*}$ and $\frac{w}{d}$ could be assumed, and that

$$E = 225.\ U^* R_h \tag{438}$$

could be used as an approximation to eliminate the need for knowledge of the velocity profile distribution.

By investigating the relationship between lateral velocity variations and the longitudinal dispersion coefficient, Fischer[42] obtained an equation which showed the importance of the lateral variation of the longitudinal velocity and the minimal effect of the lateral diffusion. Although Fischer's equation had important theoretical implications, it was too complex for practical use.

Jain[51], however, used Fischer's equation to develop his relationship. Based on Fischer's equation, Jain found that

$$E = \beta_j \frac{u^2 w^2}{e_z} \tag{439}$$

where

u = cross-sectional average value of the velocity

w = channel width

e_z = lateral diffusion coefficient

β_j = coefficient ranging from 10^{-4} to 10^{-2}. The method for calculating β_j is described by Jain[51].

In 1974, McQuivey and Keefer[52] predicted E by a simple equation using only bulk flow properties. They proposed that

$$E = 0.058 \frac{Q}{SW} \tag{440}$$

where Q is the discharge, S is the energy slope, and W is the channel width.

In 1975, Fischer[53] published a new equation in a discussion of McQuivey and Keefer's article. Fischer proposed that

$$E = 0.011 \frac{u^2 w^2}{dU^*} \tag{441}$$

where u is the mean velocity, w is the channel width, d is the mean depth, and U^* is the shear velocity.

According to Liu[54], none of the previous equations are accurate within one order of magnitude. In response, Liu showed the following formula to be able to predict E within a factor 6. Based on the best fit of certain data, Liu found that

$$E = \frac{\beta Q^2}{U^* R_h^3} \tag{442}$$

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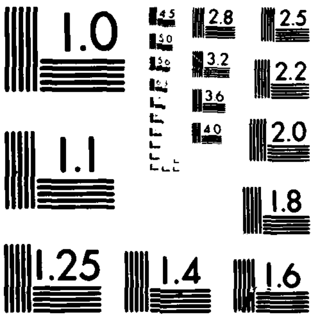

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where R_h is the hydraulic radius, and

$$\beta = 0.18\left(\frac{U^*}{u}\right)^{1.5} \tag{443}$$

Christensen [55], in a discussion of Liu's paper, re-evaluated the dimensionless parameter β based on the relationship between the two dimensionless parameters, α and β. By equating Elder's equation with Liu's equation, Christensen showed the relationship of α to β to be as follows:

$$\alpha\ d\ U^* = \frac{\beta u^2 W^3}{U^* A} \tag{444}$$

letting $h = h_m = \frac{A}{W}$:

$$\alpha = \beta\left(\frac{u}{U^*}\right)^2\left(\frac{W}{h_m}\right)^2 \tag{445}$$

By looking at Liu's mean values for α and $\frac{h_m}{W}$, Christensen found that:

$$\beta = 0.41\left(\frac{U^*}{u}\right)^2 \tag{446}$$

Liu and Dieter [56] later modified their constant to 0.4, which predicted that value of E within a factor of 4.

Using the modified Fickian theory and analyzing a larger set of data, Cheng [39] found that the coefficient should be 0.5 so that

$$E = 0.5 \frac{U^{*}A^{2}}{d^{3}} \tag{447}$$

where d replaces R_h as the mean depth flow, U^{*} is the shear velocity and A is the cross-sectional area.

This equation appears to give the most accurate value of the dispersion coefficient. One study shows that for natural streams, this equation predicts the true value of E within a factor of 2.5. Of all equations discussed this far, it appears to be the most accurate.

5. NEAR-FIELD CONTINUOUS SPILL MODEL

The method of obtaining solutions for the continuous release spill conditions involves either integrating the instantaneous point source solutions with respect to time, over the duration of release, or developing a steady state equation for long duration releases by applying the conservation of mass principle. General application of the principle of superposition, giving continuous release solutions as integrals of instantaneous release equations, for arbitrary release rate conditions is discussed in Section II. The integral approach to obtain an equation for the concentration in a non-tidal river from a continuous spill closely parallels the similar formulation for spills into still water, and the form of the equations is quite similar.

a. Integral Equation

The non-tidal river model for continuous discharges assumes that the release rate, $\dot{M}$, is constant. The spill starts at elapsed time t=0, and stops at a later time, t_{mt}. To apply the principle of superposition, the appropriate instantaneous point source equation for three dimensions, with decay, is given in Section IV, paragraph 3.c, as:

$$c(x,y,z,t) = \frac{M}{4\,(\pi)^{3/2}\sqrt{e_x\,e_y\,e_z}\;t^{3/2}}\,e^{-\frac{(x-ut)^2}{4\,e_x t}}\,e^{-kt}$$

$$\cdot\left[e^{-\frac{(y-a)^2}{4\,e_y t}} + e^{-\frac{(y-2b+a)^2}{4\,e_y t}} + e^{-\frac{(y+2b+a)^2}{4\,e_y t}}\right]$$

$$\cdot\left[e^{-\frac{z^2}{4\,e_z t}} + e^{-\frac{(z-2d)^2}{4\,e_z t}} + e^{-\frac{(z+2d)^2}{4\,e_z t}}\right] \quad . \quad (448)$$

where M is the mass of pollutant released instantaneously, x, y, z are the downstream, cross stream and vertical depth coordinates, t is elapsed time from the start of the spill, u is the mean stream velocity, 2b=w the mean width of the stream, d the depth, a represents the location of the spill point on the surface, e_x, e_y, and e_z are the respective turbulent diffusion coefficients and k is the decay coefficient representing the degradation of chemical due to chemical reaction or biological assimilation. Since in this form the boundary conditions at the surface, channel banks and bottom are generally approximately satisfied, the equation applies (to within the first order approximation) for all values of x, y, z and could be used even for large values of x instead of assuming a uniform cross-sectional distribution.

Considering the quantity of mass, M, discharged instantaneously, as a component, $\dot{M}d\tau$, of the mass being discharged continuously, the continuous spill model is obtained by adding the concentrations at the observation point from all incremental releases. The elapsed time t in the above concentration equation for an instantaneous release gives the time after a release occurring at t=0. For use in the integral expression for continuous discharges, the incremental instantaneous release occurs at time τ where τ varies from 0 (start of release) to t_{mt}, and the instantaneous concentration equation for an incremental release of $\dot{M}d\tau$ is used with $(t-\tau)$ substituted for t.

Next, it can be seen that the instantaneous equation consists of the sum of a number of similar terms, and the following short-hand notation is introduced:

$$s = 4(\pi)^{3/2}\sqrt{e_x\, e_y\, e_z} \tag{449}$$

$$\beta_1^2 = \frac{(y-a)^2}{4\, e_y}\ ,\ \beta_2^2 = \frac{(y-2b+a)^2}{4\, e_y}\ ,\ \beta_3^2 = \frac{(y+2b+a)^2}{4\, e_y} \tag{450}$$

$$\gamma_1^2 = \frac{z^2}{4\, e_z}\ ,\ \gamma_2^2 = \frac{(z-2d)^2}{4\, e_z}\ ,\ \gamma_3^2 = \frac{(z+2d)^2}{4\, e_z} \tag{451}$$

Substituting $\dot{M}d\tau$ for M, $(t-\tau)$ for t and the above notation, the concentration equation for an instantaneous release of a quantity $\dot{M}d\tau$ at time τ is written, for time $t > \tau$, as:

$$c\{x,y,z,(t-\tau)\} = \frac{\dot{M}d\tau}{s(t-\tau)^{3/2}} e^{-\frac{\{x-u(t-\tau)\}^2}{4\,e_x(t-\tau)}} e^{-k(t-\tau)}$$

$$\cdot \left[\sum_{i=1}^{3} e^{-\frac{\beta_i^2}{t-\tau}}\right] \cdot \left[\sum_{j=1}^{3} e^{-\frac{\gamma_j^2}{t-\tau}}\right] \tag{452}$$

The concentration is zero for $t < \tau$. Expanding the exponential term in x, and combining similar terms in $t-\tau$ gives the above equation as:

$$c\{x,y,z,(t-\tau)\} = \frac{\dot{M}d\tau\; e^{\frac{xu}{2e_x}}}{s(t-\tau)^{3/2}} e^{-\frac{(u^2+4e_x k)}{4\,e_x}(t-\tau)} .$$

$$\cdot\; e^{-\frac{x^2}{4\,e_x(t-\tau)}} \sum_{i=1}^{3} \sum_{j=1}^{3} e^{-\frac{(\beta_i^2+\gamma_j^2)}{t-\tau}} \tag{453}$$

Introducing further notation that:

$$\omega^2 = \frac{u^2 + 4\,e_x k}{4\,e_x} \tag{454}$$

and

$$r_{ij}^2 = \frac{x^2}{4\,e_x} + \beta_i^2 + \gamma_j^2 \tag{455}$$

The concentration equation for the instantaneous discharge integral finally is obtained in the form:

$$c\{x,y,z,(t-\tau)\} = \sum_{i=1}^{3} \sum_{j=1}^{3} e^{\frac{xu}{2e_x}} \frac{\dot{M}\, e^{-\omega^2(t-\tau)}\, e^{-\frac{r_{ij}^2}{(t-\tau)}}}{s(t-\tau)^{3/2}}\, d\tau \qquad (456)$$

The integral equation for the concentration at time t from a continuous discharge starting at time t=0 is then obtained by integrating this equation with respect to τ from $\tau=0$ to some upper limit τ_s.

The upper limit of integration is written as τ_s since the actual limit to be used depends on the relative values of the observation time, t, and the time the spill stops, t_{mt}. If t is less than t_{mt}, the integrand gives the incremental contributions from the continuous release for the complete history of the release from t=0 to t, and the limit τ_s is given by t. If t is greater than t_{mt}, then for values of τ greater than t_{mt}, at which time the spill ceases, the incremental releases do not contribute to the concentration distributions; the upper limit τ_s then becomes t_{mt}.

Since the integration is over time, the order of the integration and summation can be reversed to yield the integral equation for the concentration in a non-tidal river from a continuous discharge as:

$$c(x,y,z,t) = \frac{\dot{M}}{s}\, e^{\frac{xu}{2e_x}} \sum_{i=1}^{3} \sum_{j=1}^{3} \int_{0}^{\tau_s} \frac{e^{-\omega^2(t-\tau)}\, e^{-\frac{r_{ij}^2}{(t-\tau)}}}{(t-\tau)^{3/2}}\, d\tau \qquad (457)$$

for t > 0. The concentration c(x,y,z,t) = 0 for t < 0.

b. Analytical Evaluation

The form of the integral in the concentration equation is denoted by I, and the transformation $\xi = \frac{r_{ij}}{\sqrt{t-\tau}}$ is used to obtain:

$$I = \frac{2}{r_{ij}} \int_{\xi_0}^{\xi_s} e^{-\frac{\omega^2 r_{ij}^2}{\xi^2}} e^{-\xi^2} d\xi \tag{458}$$

where $\xi_0 = \frac{r_{ij}}{\sqrt{t}}$ and $\xi_s = \frac{r_{ij}}{\sqrt{t-\tau_s}}$

To complete the square for the expression in the exponent, the following relations are written:

$$\left(\xi + \frac{r_{ij}\omega}{\xi}\right)^2 = \xi^2 + \frac{r_{ij}^2\omega^2}{\xi^2} + 2\, r_{ij}\omega \tag{459}$$

$$\left(\xi - \frac{r_{ij}\omega}{\xi}\right)^2 = \xi^2 + \frac{r_{ij}^2\omega^2}{\xi^2} - 2\, r_{ij}\omega \tag{460}$$

and it can be seen that the sum of these terms is equal to twice the magnitude of the exponent in the integrand. Substitution gives the integral as:

$$I = \frac{2}{r_{ij}} \int_{\xi_0}^{\xi_s} \frac{1}{2} \left[e^{2r_{ij}\omega} e^{-\left(\xi + \frac{r_{ij}\omega}{\xi}\right)^2} + e^{-2r_{ij}\omega} e^{-\left(\xi - \frac{r_{ij}\omega}{\xi}\right)^2} \right] d\xi \tag{461}$$

The integrand now contains two separate terms in the form of derivatives of an error function. Forming the derivative of the error functions:

$$d\left[\operatorname{erf}\left(\xi + \frac{r_{ij}\omega}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\left(\xi + \frac{r_{ij}\omega}{\xi}\right)^2}\left(1 - \frac{r_{ij}\omega}{\xi^2}\right)d\xi \qquad (462)$$

$$d\left[\operatorname{erf}\left(\xi - \frac{r_{ij}\omega}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\left(\xi - \frac{r_{ij}\omega}{\xi}\right)^2}\left(1 + \frac{r_{ij}\omega}{\xi^2}\right)d\xi \qquad (463)$$

then multiplying the first expression by $e^{2r_{ij}\omega}$, the second by $e^{-2r_{ij}\omega}$ and summing gives:

$$e^{2r_{ij}\omega}\, d\left[\operatorname{erf}\left(\xi + \frac{r_{ij}\omega}{\xi}\right)\right] + e^{-2r_{ij}\omega}\, d\left[\operatorname{erf}\left(\xi - \frac{r_{ij}\omega}{\xi}\right)\right] =$$

$$\frac{2}{\sqrt{\pi}}\, e^{2r_{ij}\omega}\, e^{-\left(\xi + \frac{r_{ij}\omega}{\xi}\right)^2}\left(1 - \frac{r_{ij}\omega}{\xi^2}\right) d\xi$$

$$+ \frac{2}{\sqrt{\pi}}\, e^{-2r_{ij}\omega}\, e^{-\left(\xi - \frac{r_{ij}\omega}{\xi}\right)^2}\left(1 + \frac{r_{ij}\omega}{\xi^2}\right)d\xi \qquad (464)$$

Both exponential terms on the right hand side are now in the form of the exponentials in the modified integrand; however, an additional term, $\frac{r_{ij}\omega}{\xi^2}$

appears in the product. The exponential terms on the right hand side (r.h.s.) are expanded to give:

$$(\text{r.h.s.}) = \left[\left(e^{-\xi^2} e^{-\frac{r_{ij}^2\omega^2}{\xi^2}}\right)\left(1 - \frac{r_{ij}\omega}{\xi^2}\right) + \left(e^{-\xi^2} e^{-\frac{r_{ij}^2\omega^2}{\xi^2}}\right)\left(1 + \frac{r_{ij}\omega}{\xi^2}\right)\right]\frac{2}{\sqrt{\pi}}\, d\xi \tag{465}$$

The right hand side then further reduces to $\frac{4}{\sqrt{\pi}} e^{-\xi^2} e^{-\frac{r_{ij}^2\omega^2}{\xi^2}} d\xi$ which is in the form of the original integrand. Substitution then yields the following integrable form for the integral I:

$$I = \frac{2}{r_{ij}} \int_{\xi_0}^{\xi_s} \frac{\sqrt{\pi}}{4} \left\{ e^{2r_{ij}\omega}\, d\left[\operatorname{erf}\left(\xi + \frac{r_{ij}\omega}{\xi}\right)\right] + e^{-2r_{ij}\omega}\, d\left[\operatorname{erf}\left(\xi - \frac{r_{ij}\omega}{\xi}\right)\right]\right\} \tag{466}$$

Integration then gives the analytical equation for I as:

$$I = \frac{\sqrt{\pi}}{2r_{ij}} \left\{ e^{2r_{ij}\omega} \left[\operatorname{erf}\left(\xi_s + \frac{r_{ij}\omega}{\xi_s}\right) - \operatorname{erf}\left(\xi_0 + \frac{r_{ij}\omega}{\xi_0}\right)\right] + e^{-2r_{ij}\omega} \left[\operatorname{erf}\left(\xi_s - \frac{r_{ij}\omega}{\xi_s}\right) - \operatorname{erf}\left(\xi_0 - \frac{r_{ij}\omega}{\xi_0}\right)\right]\right\} \tag{467}$$

The remaining steps are to substitute the values of the limits ξ_0 and ξ_s for the two cases of interest, $t < t_{mt}$ and $t > t_{mt}$, then to evaluate the sums of the integrals over the indices i and j to satisfy boundary conditions at the river channel banks and bottom.

(1) $t < t_{mt}$

When the observation time t is less than the duration of the continuous release, the upper limit of the original integral, τ_s, is equal to t. This gives

$$\xi_0 = \frac{r_{ij}}{\sqrt{t}} \quad \text{and} \quad \xi_s = \infty \tag{468}$$

Substitution of these values for the error function arguments gives:

$$\mathrm{erf}\left(\xi_s + \frac{r_{ij}\omega}{\xi_s}\right) = 1 \tag{469}$$

$$\mathrm{erf}\left(\xi_0 + \frac{r_{ij}\omega}{\xi_0}\right) = \mathrm{erf}\left(\frac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t}\right) \tag{470}$$

$$\mathrm{erf}\left(\xi_s - \frac{r_{ij}\omega}{\xi_s}\right) = 1 \tag{471}$$

$$\mathrm{erf}\left(\xi_0 - \frac{r_{ij}\omega}{\xi_0}\right) = \mathrm{erf}\left(\frac{r_{ij}}{\sqrt{t}} - \omega\sqrt{t}\right) \tag{472}$$

and the value of the integral I for $t < t_{mt}$ becomes:

$$I = \frac{\sqrt{\pi}}{2\,r_{ij}} \left\{ e^{2r_{ij}\omega} \left[1 - \mathrm{erf}\left(\frac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t} \right) \right] \right.$$

$$\left. + e^{-2r_{ij}\omega} \left[1 - \mathrm{erf}\left(\frac{r_{ij}}{\sqrt{t}} - \omega\sqrt{t} \right) \right] \right\} \qquad (473)$$

(a) Numerical Instability

The first term in the equation for the integral I:

$$e^{2r_{ij}\omega} \left[1 - \mathrm{erf}\left(\frac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t} \right) \right] \qquad (474)$$

has an analytical limit of zero as either r_{ij} or t becomes large, although for large values of r, differences in convergence rates of the numerical approximations of the exponential and error functions give a product of these terms that is not numerically stable. From Section II.3.a.(7).(e), the modified numerical approximation for the error function is obtained as:

$$\mathrm{erf}(x) = 1 - P(b,\eta)\, e^{-x^2} \qquad \text{for } x \geq 0 \qquad (475)$$

where η is given by $\frac{1}{1+px}$ and varies from 1 to 0 as x ranges from 0 to ∞. The polynomial $P(b,\eta)$ is obtained from Hasting's approximation, and ranges in value from 1 at $x=0$ to 0 as $x \to \infty$.

Letting $\eta_{ij} = \dfrac{1}{1 + p\left(\dfrac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t} \right)}$, this form of the error function approximation is substituted to yield:

$$e^{2r_{ij}\omega}\left[1 - \operatorname{erf}\left(\frac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t}\right)\right] = e^{2r_{ij}\omega}\, P(b,\eta_{ij})\, e^{-\left(\frac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t}\right)^2}$$

$$= P(b,\eta_{ij})\, e^{-\frac{r_{ij}^2}{t} - \omega^2 t} \qquad (476)$$

In this form the exponential $e^{2r_{ij}\omega}$ has been removed, and the entire expression is obtained in the form of a stable decaying exponential.

By substitution, the preferred form of the equation for the integral I is then obtained as:

$$I = \frac{\sqrt{\pi}}{2r_{ij}}\left\{P(b,\eta_{ij})\, e^{-\frac{r_{ij}^2}{t} - \omega^2 t} + e^{-2r_{ij}\omega}\left[1 - \operatorname{erf}\left(\frac{r_{ij}}{\sqrt{t}} - \omega\sqrt{t}\right)\right]\right\} \qquad (477)$$

(b) Concentration Equation

Using the expression for the integral I, the entire equation for the concentration as a function of time and distance is obtained by summing over the indices i and j, by substitution in the equation:

$$c(x,y,z,t) = \frac{\dot{M}}{s}\, e^{\frac{xu}{2e_x}} \sum_{i=1}^{3} \sum_{j=1}^{3} I \qquad (478)$$

where the term I is a function of r_{ij}.

(c) Limit Behavior

In the limit as the distance from the spill location becomes small, the values of the distance terms r_{ij} will approach limit values determined by the dimensions of the river channel, and the location of the spill relative to the channel center line, and one of these terms will become zero. The corresponding value of the integral I for $r_{ij} \to 0$ then behaves as

$$I = \frac{\sqrt{\pi}}{2r_{ij}} \left[1 - \text{erf}\ (\omega\sqrt{t}) + 1 - \text{erf}\ (-\omega\sqrt{t}) \right] \qquad (479)$$

Since erf $(-\omega\sqrt{t}) = -\text{erf}\ (+\omega\sqrt{t})$, the error function terms cancel, giving the result:

$$I = \frac{\sqrt{\pi}}{r_{ij}} \qquad (480)$$

and the contribution to the overall concentration distribution of this term is:

$$\Delta c = \frac{\dot{M}}{s}\, e^{\frac{xu}{2e_x}} \frac{\sqrt{\pi}}{r_{ij}} = \frac{\dot{M}\sqrt{\pi}}{s\ r_{ij}} \qquad \text{for } x \to 0. \qquad (481)$$

Thus the concentration as $r_{ij} \to 0$ is independent of time and infinite. This suggests an appropriate modification of the continuous discharge equation, in a form similar to that used previously, that is, adding a term to the denominator such that the concentration at the origin is constrained to be equal to a pre-specified value. Alternatively, the concentrations computed from the equation containing the singularity can be constrained so as not to exceed the pre-specified value.

(d) Longitudinal Dispersion Neglected

If the longitudinal dispersion coefficient, e_x, is considered to be vanishingly small in the formulation for the concentration as a function of time and distance, it can be shown that the value of the integral I, taken as a function of time, reduces to one of two values, both of which are independent of time. Thus the condition of neglecting the longitudinal dispersion reduces the time dependent concentration equation to the steady state case.

The limit values obtained as $e_x \to 0$ are:

$$I = \frac{\sqrt{\pi}}{r_{ij}} e^{-2r_{ij}\omega} \qquad \text{for } \frac{r_{ij}}{\sqrt{t}} < \omega t \tag{482}$$

$$I = 0 \qquad \text{for } \frac{r_{ij}}{\sqrt{t}} > \omega\sqrt{t} \tag{483}$$

That is, neglecting the longitudinal dispersion e_x gives a steady state solution such that, at any fixed point r_{ij} the concentration is zero for all values of time less than $\frac{r_{ij}}{\omega}$. The concentration distribution then has a discontinuity, rising immediately to the steady state value for times greater than $\frac{r_{ij}}{\omega}$.

(e) Steady State Equation

For a continuous discharge which emits indefinitely, the concentration distribution which results is obtained by taking the limit as t → ∞. Denoting the steady state value of the integral I as I_{ss}, taking the limit as t becomes large reduces the error function terms to give:

$$I_{ss} = \frac{\sqrt{\pi}}{r_{ij}} e^{-2r_{ij}\omega} \tag{484}$$

The complete steady state concentration distribution is then given by:

$$c(x,y,z) = \frac{\dot{M}}{s} e^{\frac{xu}{2e_x}} \sum_{i=1}^{3} \sum_{j=1}^{3} I_{ss} \tag{485}$$

$$c(x,y,z) = \frac{\dot{M}\sqrt{\pi}}{s} e^{\frac{xu}{2e_x}} \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{1}{r_{ij}} e^{-2r_{ij}\omega} \tag{486}$$

where s, r_{ij} and ω are as defined previously, and the longitudinal dispersion e_x has not been neglected.

(i) Negligible e_x

If the longitudinal dispersion coefficient is considered to be vanishingly small, the corresponding form of the steady state concentration distribution can be obtained by substituting the expressions for s, r_{ij} and ω, then taking the limit as $e_x \to 0$.

Using

$$s = 4(\pi)^{3/2}\sqrt{e_x\, e_y\, e_z} \tag{487}$$

and rearranging terms, gives for the steady state concentration distribution:

$$c(x,y,z) = \frac{\dot{M}}{4\pi\sqrt{e_y e_z}} \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{1}{\sqrt{e_x}\, r_{ij}}\, e^{\frac{xu}{2e_x}}\, e^{-2r_{ij}\omega} \qquad (488)$$

Using $r_{ij}^2 = \frac{x^2}{4e_x} + \beta_i^2 + \gamma_j^2$, the term in the denominator can be written as:

$$\sqrt{e_x}\, r_{ij} = \sqrt{e_x}\left[\frac{x^2}{4e_x} + \beta_i^2 + \gamma_j^2\right]^{1/2} \qquad (489)$$

$$\sqrt{e_x}\, r_{ij} = \frac{\sqrt{e_x}}{\sqrt{e_x}}\left[\frac{x^2}{4} + e_x\,\beta_i^2 + e_x\,\gamma_j^2\right]^{1/2} \qquad (490)$$

which in the limit as $e_x \to 0$ reduces to $\frac{x}{2}$.

Next, using $\omega^2 = \frac{u^2+4e_x k}{4e_x} = \frac{u^2}{4e_x}\left(1 + \frac{4e_x k}{u^2}\right)$ then $\omega = \frac{u}{2\sqrt{e_x}}\left(1 + \frac{4e_x k}{u^2}\right)^{1/2}$. For e_x small, the approximation $\left(1 + \frac{4e_x k}{u^2}\right)^{1/2} \simeq 1 + \frac{1}{2} \cdot \frac{4e_x k}{u^2}$ to give for ω:

$$\omega = \frac{u}{2\sqrt{e_x}}\left(1 + \frac{2e_x k}{u^2}\right) \qquad (491)$$

Similarly for r_{ij},

$$r_{ij} = \frac{x}{2\sqrt{e_x}}\left[1 + \frac{4e_x}{x^2}\left(\beta_i^2 + \gamma_j^2\right)\right]^{1/2} \qquad (492)$$

$$r_{ij} \cong \frac{x}{2\sqrt{e_x}} \left[1 + \frac{1}{2} \frac{4e_x}{x^2} \left(\beta_i^2 + \gamma_j^2 \right) \right] \qquad (493)$$

Combining terms then gives for the exponential terms in the concentration equation:

$$e^{\frac{xu}{2e_x}} e^{-2r_{ij}\omega} = e^{\frac{xu}{2e_x}} e^{-\frac{2x}{2\sqrt{e_x}} \left[1 + \frac{2e_x}{x^2} \left(\beta_i^2 + \gamma_j^2 \right) \right] \frac{u}{2\sqrt{e_x}} \left(1 + \frac{2e_x k}{u^2} \right)} \qquad (494)$$

Expanding the right hand side simplifies the expression to:

$$e^{\frac{xu}{2e_x}} e^{-2r_{ij}\omega} = e^{-\frac{xk}{u}} e^{-\frac{u}{x}\left(\beta_i^2 + \gamma_j^2 \right)} e^{-\frac{2e_x k}{x}\left(\beta_i^2 + \gamma_j^2 \right)} \qquad (495)$$

and in the limit as e_x becomes small, the last exponential term on the right becomes unity.

Substituting the above limit values gives the equation for the steady state concentration when the longitudinal dispersion coefficient e_x is vanishingly small as:

$$c(x,y,z) = \frac{\dot{M}}{2\,\pi\, x\sqrt{e_y e_z}} e^{-\frac{xk}{u}} \sum_{i=1}^{3} \sum_{j=1}^{3} e^{-\frac{u}{x}\left(\beta_i^2 + \gamma_j^2 \right)} \qquad (496)$$

(2) $t > t_{mt}$

When the observation time t is greater than the duration of the continuous release, the upper limit of the original integral I, τ_s, is equal to t_{mt}. This gives $\xi_0 = \frac{r_{ij}}{\sqrt{t}}$ and $\xi_s = \frac{r_{ij}}{\sqrt{t-t_{mt}}}$. Substitution of the value for ξ_s in the appropriate error function arguments of the expression for the integral I gives:

$$\text{erf}\left(\xi_s + \frac{r_{ij}\omega}{\xi_s}\right) = \text{erf}\left(\frac{r_{ij}}{\sqrt{t-t_{mt}}} + \omega\sqrt{t-t_{mt}}\right) \tag{497}$$

$$\text{erf}\left(\xi_s - \frac{r_{ij}\omega}{\xi_s}\right) = \text{erf}\left(\frac{r_{ij}}{\sqrt{t-t_{mt}}} - \omega\sqrt{t-t_{mt}}\right) \tag{498}$$

and the equation for the integral I becomes:

$$I = \frac{\sqrt{\pi}}{2r_{ij}}\left\{e^{2r_{ij}\omega}\left[\text{erf}\left(\frac{r_{ij}}{\sqrt{t-t_{mt}}} + \omega\sqrt{t-t_{mt}}\right) - \text{erf}\left(\frac{r_{ij}}{\sqrt{t}} + \omega\sqrt{t}\right)\right]\right.$$
$$\left. + e^{-2r_{ij}\omega}\left[\text{erf}\left(\frac{r_{ij}}{\sqrt{t-t_{mt}}} - \omega\sqrt{t-t_{mt}}\right) - \text{erf}\left(\frac{r_{ij}}{\sqrt{t}} - \omega\sqrt{t}\right)\right]\right\} \tag{499}$$

The equation for the concentration is the same as for the case $t < t_{mt}$ except that the above value of I is used.

As t becomes large, the error function terms in the integral I vanish, and thus the concentrations also become zero. For large values of r_{ij}, however, the first term in the integral expression exhibits the same type of instability as before, and for computational use the error function terms are replaced by appropriate expressions from Hasting's approximation. Also, the expression as written for I cannot be used at the spill location $r_{ij}=0$ without a modification, described previously, such that the concentration at the origin remains finite.

c. Alternate Derivation of Steady State Equation[18]

The form of the concentration distribution equation for a spill into a non-tidal river, in which the longitudinal dispersion coefficient e_x is neglected, may also be derived in a simplified manner. It is assumed that the distribution in any y-z plane perpendicular to the flow along the x axis is Gaussian so that the function

$$F = e^{-\frac{y^2}{2\sigma_y^2}} e^{-\frac{z^2}{2\sigma_z^2}} \tag{500}$$

is used to obtain scale factors between concentrations at (x,0,0) and at (x,y,z). This scale function has a value of unity along the x axis, values less than 1 for $y > 0$ and $z > 0$ at any x, and determines the ratio of the concentration at any location to the concentration at the location of the x axis in the y-z plane:

$$\frac{c(x,y,z,t)}{c(x,0,0,t)} = F \tag{501}$$

At any location, or instant of time, the standard deviations are determined by the dispersion coefficients and time so the function F may in general depend on both time and distance.

Conservation of mass, when the longitudinal dispersion e_x is neglected, then requires that the flow rate of substance through any plane perpendicular to the x-axis remains constant, and equal to the rate at which the substance is discharging, $\dot{M}$. Since the discharge rate $\dot{M}$ is assumed to be constant with respect to time, then conservation of mass for e_x negligible requires that the flow rate at any location x also be independent of time. However, σ_y and σ_z may be taken as functions of distance x.

The incremental flow rate through an element of area dA normal to the x axis at a location x,y,z is given by c(x,y,z) u dA.

The integral of this rate over the area, by conservation of mass, is equal to the discharge rate $\dot{M}$, which gives the following:

$$\dot{M} = \int c(x,y,z)\ u\ dA \tag{502}$$

Substituting the function F to express the concentration at (x,y,z) in terms of the concentration at (x,0,0) gives:

$$\dot{M} = \int_0^\infty \int_{-\infty}^\infty u \cdot c(x,0,0)\ e^{-\frac{y^2}{2\sigma_y^2}}\ e^{-\frac{z^2}{2\sigma_z^2}}\ dy\ dz \tag{503}$$

where the integral is evaluated over a semi-infinite area extending for all values of y, and values of z > 0. For simplicity, the image sources to account for the river channel constraints and the decay term are omitted.

Since the value of the integral is constant over time for any location x, the standard deviations σ_y and σ_z are obtained as functions of distance, x, by substituting $t = \frac{x}{u}$ in

$$\sigma_y = \sqrt{2e_y t} = \frac{\sqrt{2e_y x}}{\sqrt{u}} \tag{504}$$

$$\sigma_z = \sqrt{2e_z t} = \frac{\sqrt{2e_z x}}{\sqrt{u}} \tag{505}$$

The expression for conservation of mass then becomes:

$$\dot{M} = u \cdot c(x,0,0) \int_0^\infty e^{-\frac{z^2 u}{4e_z x}} dz \int_{-\infty}^{\infty} e^{-\frac{y^2 u}{4e_y x}} dy \tag{506}$$

The integrals are evaluated using the definition of the error function to obtain:

$$\dot{M} = u \cdot c(x,0,0) \left(\frac{2\sqrt{e_z x}}{\sqrt{u}} \cdot \frac{\sqrt{\pi}}{2} \right) \cdot \left(\frac{2\sqrt{e_y x}}{\sqrt{u}} \cdot \frac{2\sqrt{\pi}}{2} \right) \tag{507}$$

Simplifying and solving this equation for c(x,0,0) gives:

$$c(x,0,0) = \frac{\dot{M}}{2\,\pi\, x\sqrt{e_y e_z}} \tag{508}$$

This result is then substituted in the concentration ratio using the Gaussian distribution F to obtain the final form of the equation for the concentration at any point x,y,z:

$$c(x,y,z) = \frac{\dot{M}}{2\,\pi\,x\sqrt{e_y e_z}}\, e^{-\frac{y^2 u}{4 e_y x}}\, e^{-\frac{z^2 u}{4 e_z x}} \tag{509}$$

It can be seen that this equation has the same form as that derived from the more general time dependent concentration equation in the limit as the longitudinal dispersion coefficient e_x vanishes. This equation gives the concentration as a function of spatial coordinates x,y,z only and not time. The values of c(x,y,z) are in fact the steady state concentrations resulting from a continuous discharge of infinite duration with the additional assumption that the longitudinal dispersion e_x is neglected. Since the concentration is obtained independently of time, the initial period at any location x,y,z during which the concentration increases from 0 to the steady state value (rise time) is also neglected in this formulation. Thus this approach gives the result that $c(x,y,z,t)=0$ for $t < \frac{x}{u}$ and $c(x,y,z,t) =$ steady state value for $t > \frac{x}{u}$ at any location x. For a continuous discharge of a finite duration t_{mt}, the steady state distribution can be somewhat crudely applied to estimate the concentration at a location x during the time interval $t = \frac{x}{u}$ to $t = \frac{x}{u} + t_{mt}$. For times less than $\frac{x}{u}$ or greater than $\frac{x}{u} + t_{mt}$, the concentration at the point x is taken as zero.

It should be noted that the above form of the concentration equation is similar to equations used for vapor dispersion.

d. Cross-Sectional Variation of Steady State Concentration

Incorporating the first order image terms gives the complete equation for a continuous discharge into a non-tidal river, under steady state contions, as:

$$c(x,y,z) = \frac{\dot{M}}{2\,\pi\,x\sqrt{e_y e_z}}\, e^{-\frac{kx}{u}} \cdot$$

$$\left[e^{-\frac{u(y-a)^2}{4\,x\,e_y}} + e^{-\frac{u(y-2b+a)^2}{4\,x\,e_y}} + e^{-\frac{u(y+2b+a)^2}{4\,x\,e_y}} \right] \cdot$$

$$\left[e^{-\frac{uz^2}{4\,x\,e_z}} + e^{-\frac{u(z-2d)^2}{4\,x\,e_x}} + e^{-\frac{u(z+2d)^2}{4\,x\,e_y}} \right] \qquad (510)$$

For the special case of a spill at the centerline of the river, a=0, the two functions in the above, one in y and one in z, expressing the cross-sectional variation in concentration, have the identical form. That is, if a function G is defined as:

$$G(y,e_y,b) = e^{-\frac{uy^2}{4\,x\,e_y}} + e^{-\frac{u(y-2b)^2}{4\,x\,e_y}} + e^{-\frac{u(y+2b)^2}{4\,x\,e_y}} \qquad (511)$$

then, for a=0, the equation for the concentration can be written as:

$$c(x,y,z) = \frac{\dot{M}}{2\,\pi\,x\sqrt{e_y e_z}}\, e^{-\frac{kx}{u}} \cdot G(y,e_y,b) \cdot G(z,e_z,d) \qquad (512)$$

The function G contains three exponential functions, one corresponding to the source location at y=0 (and z=0) and two to each of the two first order image reflections. As the distance from the spill location increases, the relative contribution from each of these terms will vary depending both on the distance from the spill point and the position in the channel cross-section relative to the spill location (at the origin) at which the concentrations are computed.

At large distances from a continuous spill, under steady state conditions, the concentration is expected to be uniform across the channel cross-section and independent of the cross-channel position selected for observation. Implications of this assumption are illustrated by examining selected variations in the values of the function $G(y,e_y,b)$ for the special, and symmetrical, case of a spill at the river centerline.

Letting $\beta = e^{-\frac{ub^2}{4\ x\ e_y}}$ and selecting values of y at 0, $\frac{b}{2}$ and b gives:

$$G(0,e_y,b) = 1 + \beta^4 + \beta^4 \tag{513}$$

$$G\left(\frac{b}{2},e_y,b\right) = \beta^{\frac{1}{4}} + \beta^{\frac{9}{4}} + \beta^{\frac{25}{4}} \tag{514}$$

$$G(b,e_y,b) = \beta + \beta + \beta^9 \tag{515}$$

where β varies from 0 to 1 as x varies from 0 to ∞. Computed values of these functions are given in Table 4 for the range of β.

TABLE 4. SELECTED VALUES OF CROSS-SECTIONAL DISTRIBUTION FUNCTIONS

Distance Parameters		Function $G(y,e_y,b)$ at			Ratio:
$\beta = e^{-\frac{ub^2}{4 x e_y}}$	$\frac{xe_y}{ub^2}$	$y = 0$	$y = \frac{b}{2}$	$y = b$	$\frac{G(y=b,e_y,b)}{G(y=0,e_y,b)}$
0.0	0.0	1.00	0.0	0.0	0.0
0.1	0.11	1.00	0.56	0.20	0.20
0.2	0.16	1.00	0.70	0.40	0.40
0.3	0.21	1.02	0.81	0.60	0.59
0.4	0.27	1.05	0.92	0.80	0.76
0.5	0.36	1.12	1.06	1.00	0.89
0.6	0.49	1.26	1.24	1.21	0.96
0.7	0.70	1.48	1.47	1.44	0.97
0.8	1.12	1.82	1.80	1.73	0.95
0.9	2.37	2.31	2.28	2.19	0.95
1.0	∞	3.00	3.00	3.00	1.00

For observations along the centerline of the river (y=0), downstream from the spill, the function $G(0,e_y,b)$ has an initial value of 1.0. Little effect is initially caused by the image sources since for small values of β, $\beta^4 << 1$, so that the function value remains essentially constant at 1 until β reaches values of 0.3 to 0.4. For longer distances, the effects of the image sources become significant and the function value increases to 3 over the range $\beta = 0.4$ to $\beta = 1.0$.

For observations along the channel bank (y=b), downstream from a spill occurring at the centerline of the river, the function $G(b,e_y,b)$ has an initial value of 0. The value of the function increases almost linearly for values of β up to approximately 0.6. Over this range, the contribution of the image reflection about the opposite bank (at $y = -b$) is very small; due to symmetry, the source term and the image reflection about the bank y=b each contribute equally, with values equal to β, so the linear variation predominates. Above $\beta = 0.6$, the influence of the far image reflection becomes more pronounced, and the function value increases to 3 over the range $\beta = 0.6$ to 1.0.

At the point in the channel mid-way between the centerline and the bank, for a spill at the centerline, the difference in relative distances between the observation point and each source or image location creates three different zones of influence for values of the function $G(\frac{b}{2},e_y,b)$. Initially the value is zero, and the effects of the source term $(\beta^{1/4})$ predominate so the function value quickly rises to 0.56 for $\beta = 0.1$. Over the interval from $\beta = 0.1$ to $\beta = 0.5$, the contribution of both the source term and the image reflection about the near bank at y=b are significant, and the value of the function increases, at a reduced rate from 0.56 to

1.06. Above values of β near 0.5, the effects of the image reflection about the far bank become significant and together with the other terms cause a more rapid rise to a final value of 3.0 at $\beta = 1.0$.

Finally it can be observed that the ratio of the function G (and therefore also concentration at the surface) at the bank to the value along the centerline rises nearly linearly from a value of 0 to a value of nearly 0.9 at $\beta = 0.5$. For distances beyond $\beta = 0.5$, this ratio increases much more slowly until the final value of 1.0 is reached only at the limiting value of $\beta = 1.0$.

(1) Variation with Depth

Since for the special case of a spill at the centerline of the river, the concentrations obtained from the complete steady state equation have the same functional variation in z as in y, so the behavior of the cross-sectional variation of the function $G(z,e_z,d)$ is, except for the different parameters of the function, identical to the behavior of $G(y,e_y,d)$. The resulting concentration at any point in the cross-section however is determined by the product of these functions, so the final concentration distribution behaves accordingly.

(2) Concentrations at Limit Values

The criteria for the distance required for complete mixing to take place is given as

$$x_c = 0.3\,\frac{b^2 u}{e_y}\,, \qquad \text{or} \qquad x_c = 0.3\,\frac{d^2 u}{e_z} \tag{516}$$

That is, for values of $x < x_c$, the near field approximation is used to compute $c(x,y,z)$. For values of $x > x_c$, uniform cross-sectional distribution is assumed and only cross-sectional average concentrations are computed as $c(x)$. At this limit, the corresponding value of β computed from

$$\beta_c = e^{-\frac{ub^2}{4\, x_c\, e_y}} \tag{517}$$

is obtained as $\beta_c = 0.43$, and the corresponding values of the function G are approximately:

$$G_c(0, e_y, b) = 1.07 \tag{518}$$

$$G_c\left(\frac{b}{2}, e_y, b\right) = 0.97 \tag{519}$$

$$G_c(b, e_y, b) = 0.86 \tag{520}$$

Thus the concentrations are:

$$c(x_c, 0, z) = \frac{\dot{M}}{2\pi x_c \sqrt{e_y e_z}}\, e^{-\frac{kx_c}{u}} \cdot 1.07 \cdot G(z, e_z, d) \tag{521}$$

$$c\left(x_c, \frac{b}{2}, z\right) = \frac{\dot{M}}{2\pi x_c \sqrt{e_y e_z}}\, e^{-\frac{kx_c}{u}} \cdot 0.97 \cdot G(z, e_z, d) \tag{522}$$

$$c(x_c,b,z) = \frac{\dot{M}}{2\pi x_c\sqrt{e_y e_z}} e^{-\frac{kx_c}{u}} \cdot 0.86 \cdot G(z,e_z,d) \qquad (523)$$

It should be noted that since the cross-sectional variation in concentration obtained from the near-field solution is dependent on the product $G(y,e_y,b) \cdot G(z,e_z,d)$, then the near field solution approaches a uniform distribution only at the limit $\beta = 1$. Also, referring to Table 4, and comparing the relative concentrations across a cross-sectional segment, the limit condition could be extended to values of β of approximately 0.6, or x_c approximately $0.5 \frac{ub^2}{e_y}$.

(3) General Conditions

Depending on the river channel configuration, either transverse or vertical mixing will occur at a faster rate than the other, that is, for

$x > 0.3 \frac{ub^2}{e_y}$, transverse dispersion is assumed to be approximately uniform, and

for

$x > 0.3 \frac{ud^2}{e_z}$, vertical dispersion is assumed to be uniform.

In the preceding discussion, the spill location was assumed to be at the centerline, at an equal distance from each bank. Taking the critical distance x_c as a function of the distance between the spill location and the farthest bank gives, for spills located at an offset a from the river centerline the criteria

$$x_c = 0.3\,\frac{u(b-a)^2}{e_y}\ ,\ 0.3\,\frac{u(b+a)^2}{e_y} \tag{524}$$

In order for the limiting value x_c to be applied as a criteria for approximate uniform mixing both transversely and vertically, then the largest value of x_c should be selected:

$$x_c = \mathrm{MAX}\left\{0.3\,\frac{ud^2}{e_z},\ 0.3\,\frac{u(b+a)^2}{e_y},\ 0.3\,\frac{u(b-a)^2}{e_y}\right\} \tag{525}$$

6. FAR-FIELD CONTINUOUS SPILL MODEL

According to the criteria established in Section IV.2.d and IV.5.d, at distances sufficiently far from the spill location, the discharging chemical can be considered to have become uniformly distributed across the cross-section of the river channel. Further dispersion takes place longitudinally and is described by a one-dimensional model.

To obtain the appropriate solution for a continuous discharge, the principle of superposition is applied, obtaining the concentration distribution for a continuous discharge by integrating, over time, the concentrations from a series of instantaneous discharges.

The approximate concentration equation for an instantaneous discharge was obtained in Section IV.4 as:

$$c(x,t) = \frac{M}{2A\sqrt{\pi}\sqrt{Et}}\,e^{-\frac{(x-ut)^2}{4Et}}\,e^{-kt} \tag{526}$$

and was shown to satisfy both conservation of mass and the one-dimensional diffusion equation of the form:

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = E\frac{\partial^2 c}{\partial x^2} - kc \qquad (527)$$

In the above equation c is the cross-sectional average concentration as a function of distance from the spill location x, and elapsed time from the start of the spill, t. The characteristics of the solution to the one-dimensional diffusion equation for both instantaneous and continuous releases are described extensively in Section II of this report.

a. Integral Equation

To apply the principle of superposition, the incremental quantity of mass released instantaneously is written as $\dot{M}d\tau$. The time that this quantity is discharged is taken to be τ, and the elapsed times in the instantaneous equation are written as $(t-\tau)$ instead of t.

Substituting $\dot{M}d\tau$ for M, and $(t-\tau)$ for t, then the equation for the far field concentration from a continuous discharge can be written as the integral with respect to τ of the instantaneous equation:

$$c(x,t) = \int_0^{\tau_s} \frac{\dot{M}d\tau}{2A\sqrt{\pi}\sqrt{E(t-\tau)}}\, e^{-\frac{\{x-u(t-\tau)\}^2}{4E(t-\tau)}}\, e^{-k(t-\tau)} \qquad (528)$$

where the continuous discharge starts at time t=0. As with the near field continuous model, the upper limit of integration is written as τ_s since the actual limit to be used depends on the relative values of the observation time, t, and the time the spill stops, t_{mt}. If t is less than t_{mt}, then $\tau_s = t$. If t is greater than t_{mt}, then $\tau_s = t_{mt}$. In the above formulation, the concentration is taken to be zero for all $t < 0$.

b. Analytical Evaluation

Expanding the exponential term in x, combining similar terms in $(t-\tau)$ and factoring out constants, gives the expression for the concentration as:

$$c(x,t) = \frac{\dot{M}\, e^{\frac{xu}{2E}}}{2A\sqrt{\pi}\sqrt{E}} \int_0^{\tau_s} e^{-\frac{x^2}{4E(t-\tau)}}\, e^{-(u^2+4kE)\frac{(t-\tau)}{4E}}\, \frac{d\tau}{\sqrt{t-\tau}} \qquad (529)$$

Letting $\Omega^2 = u^2 + 4kE$, and applying the transformation $\xi = \frac{x}{\sqrt{4E(t-\tau)}}$ leads to:

$$c(x,t) = \frac{\dot{M}\, e^{\frac{xu}{2E}}}{2A\sqrt{\pi}\sqrt{E}} \cdot \frac{x}{\sqrt{E}} \cdot \int_{\xi_0}^{\xi_s} e^{-\xi^2}\, e^{-\left(\frac{\Omega x}{4E}\right)^2 \frac{1}{\xi^2}}\, \frac{d\xi}{\xi^2} \qquad (530)$$

where $\xi_0 = \frac{x}{2\sqrt{E}\sqrt{t}}$ and $\xi_s = \frac{x}{2\sqrt{E}\sqrt{t-\tau_s}}$. In this form the integral is quite similar to the concentration integral expression obtained for the near field case. For the near field solution the integrand was found to be composed of the sum of the derivatives of two error functions, and the solution for the far-field case is similarly obtained.

Letting β denote $\frac{\Omega x}{4E}$, and forming the derivatives of the error functions, as for the near field equations, gives the relations:

$$d\left[\mathrm{erf}\left(\xi + \frac{\beta}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\left(\xi + \frac{\beta}{\xi}\right)^2} \left(1 - \frac{\beta}{\xi^2}\right) d\xi \tag{531}$$

$$d\left[\mathrm{erf}\left(\xi - \frac{\beta}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\left(\xi - \frac{\beta}{\xi}\right)^2} \left(1 + \frac{\beta}{\xi^2}\right) d\xi \tag{532}$$

Multiplying the first expression by $e^{2\beta}$ and expanding the exponential term on the right hand side gives:

$$e^{2\beta}\, d\left[\mathrm{erf}\left(\xi + \frac{\beta}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\xi^2}\, e^{-\frac{\beta^2}{\xi^2}}\, d\xi - \frac{2\beta}{\sqrt{\pi}}\, e^{-\xi^2}\, e^{-\frac{\beta^2}{\xi^2}} \frac{d\xi}{\xi^2} \tag{533}$$

where the last term is in the same form as the integrand in the concentration integral.

Multiplying the second error function derivative by $e^{-2\beta}$ and expanding the exponential term on the right hand side similarly leads to:

$$e^{-2\beta}\, d\left[\mathrm{erf}\left(\xi - \frac{\beta}{\xi}\right)\right] = \frac{2}{\sqrt{\pi}}\, e^{-\xi^2}\, e^{-\frac{\beta^2}{\xi^2}}\, d\xi + \frac{2\beta}{\sqrt{\pi}}\, e^{-\xi^2}\, e^{-\frac{\beta^2}{\xi^2}} \frac{d\xi}{\xi^2} \tag{534}$$

Next, taking the difference of these equations (instead of the sum as for the near field case), and multiplying $\frac{\sqrt{\pi}}{4\beta}$, gives

$$e^{-\xi^2} e^{-\frac{\beta^2}{\xi^2}} \frac{d\xi}{\xi^2} = \frac{\sqrt{\pi}\, e^{-2\beta}}{4\beta}\, d\left[\operatorname{erf}\left(\xi - \frac{\beta}{\xi}\right)\right]$$

$$- \frac{\sqrt{\pi}\, e^{2\beta}}{4\beta}\, d\left[\operatorname{erf}\left(\xi + \frac{\beta}{\xi}\right)\right] \qquad (535)$$

This result gives the integrand of the concentration equation as a sum of two derivatives of error functions, and the closed form expression for the concentration integral can be written directly as:

$$c(x,t) = \frac{\dot{M}\, e^{\frac{xu}{2E}}}{2A\sqrt{\pi}\sqrt{E}} \cdot \frac{x}{\sqrt{E}} \cdot$$

$$\left\{\frac{\sqrt{\pi}\, e^{-2\beta}}{4\beta} \operatorname{erf}\left(\xi - \frac{\beta}{\xi}\right) - \frac{\sqrt{\pi}\, e^{2\beta}}{4\beta} \operatorname{erf}\left(\xi + \frac{\beta}{\xi}\right)\right\}_{\xi_0}^{\xi_s} \qquad (536)$$

Combining terms, replacing β and ξ, substituting the limits of integration and changing the signs of the error function terms gives the general form of the concentration equation as:

$$c(x,t) = \frac{\dot{M}}{2A\Omega} e^{\frac{xu}{2E}} \left\{ e^{\frac{\Omega x}{2E}} \left[\mathrm{erf}\left(\frac{x+\Omega t}{\sqrt{4Et}}\right) - \mathrm{erf}\left(\frac{x+\Omega(t-\tau_s)}{\sqrt{4E(t-\tau_s)}}\right)\right]\right.$$

$$\left. - e^{-\frac{\Omega x}{2E}} \left[\mathrm{erf}\left(\frac{x-\Omega t}{\sqrt{4Et}}\right) - \mathrm{erf}\left(\frac{x-\Omega(t-\tau_s)}{\sqrt{4E(t-\tau_s)}}\right)\right]\right\} \qquad (537)$$

The remaining step is to substitute the value of the limit τ_s for the two cases of interest, $t < t_{mt}$ and $t > t_{mt}$.

(1) $t < t_{mt}$

When the observation time t is less than the duration of the continuous release, the upper limit of the original integral, τ_s, is equal to t. This gives

$$\mathrm{erf}\left(\frac{x+\Omega(t-\tau_s)}{\sqrt{4E(t-\tau_s)}}\right) = 1 \quad \text{at } \tau_s = t \qquad (538)$$

$$\mathrm{erf}\left(\frac{x-\Omega(t-\tau_s)}{\sqrt{4E(t-\tau_s)}}\right) = 1 \quad \text{at } \tau_s = t \qquad (539)$$

and the equation for the concentration becomes

$$c(x,t) = \frac{\dot{M}}{2A\Omega} e^{\frac{xu}{2E}} \left\{ e^{\frac{\Omega x}{2E}} \left[\operatorname{erf}\left(\frac{x+\Omega t}{\sqrt{4Et}} \right) - 1 \right] - e^{-\frac{\Omega x}{2E}} \left[\operatorname{erf}\left(\frac{x-\Omega t}{\sqrt{4Et}} \right) - 1 \right] \right\} \tag{540}$$

for $0 < t < t_{mt}$. The concentration $c(x,t)$ is zero for $t < 0$.

(a) Numerical Instability

At very large times or distances, the equation for the concentration approaches an analytical limit of zero. However, as was the case with the near-field solution, for very large values of x, differences in convergence rates of the numerical approximations of the exponential and error functions give a product of these terms that is not numerically stable. For numerical computation, the results of section II.3.a.(7).(e) should be applied to express the first error function term in the modified form using Hasting's approximation. This leads to an expression for the concentration in which all exponential terms have negative exponents, and the numerical instability is removed.

(b) Steady State Equation

For a continuous discharge which emits indefinitely, the concentration distribution which results is obtained by taking the limit as $t \to \infty$. For the case $t < t_{mt}$, the limit values of the error function terms become:

$$\lim_{t \to \infty} \operatorname{erf}\left(\frac{x+\Omega t}{\sqrt{4Et}} \right) = 1 \tag{541}$$

$$\lim_{t\to\infty} \operatorname{erf}\left(\frac{x-\Omega t}{\sqrt{4Et}}\right) = -1 \tag{542}$$

and the equation for the steady state concentration distribution becomes:

$$c(x) = \frac{\dot{M}}{A\Omega}\, e^{-\frac{x}{2E}(\Omega-u)} \tag{543}$$

Since $\Omega = \sqrt{u^2+4kE}$, then $\Omega \geqslant u$, and the steady state concentration profile is obtained as a decaying exponential function in x; the numerical instability appearing in the time dependent equation for c(x,t) is removed.

Expanding the term in the exponent as:

$$\frac{x}{2E}(\Omega-u) = \frac{x}{2E}\left[\sqrt{u^2+4kE} - u\right] = \frac{x}{2E}\left[u\sqrt{1+\frac{E}{u^2/4k}} - u\right] \tag{544}$$

it can be seen that if the longitudinal dispersion coefficient E is very much smaller than $u^2/4k$, then the following approximation can be applied:

$$\left(1+\frac{E}{u^2/4k}\right)^{1/2} \cong 1 + \frac{1}{2}\cdot\frac{E}{u^2/4k} \tag{545}$$

and, for this condition, the exponent becomes

$$\frac{x}{2E}(\Omega-u) = \frac{x}{2E}\left[u\left(1+\frac{1}{2}\cdot\frac{E}{u^2/4k}\right) - u\right] = \frac{xk}{u} \tag{546}$$

Since $E << \frac{u^2}{4k}$ then

$$\Omega \cong u \left(1 + \frac{1}{2} \frac{E}{u^2/4k} \right) \tag{547}$$

and neglecting the second term gives $\Omega = u$. The steady state concentration distribution for this case is then given by:

$$c(x) = \frac{\dot{M}}{Au} e^{-\frac{xk}{u}}, \qquad E << \frac{u^2}{4k} \tag{548}$$

(c) Limit Behavior

Depending on the magnitude of the terms $\dot{M}$, A, Ω, the steady state concentration is not limited, i.e., the density of the chemical may be exceeded. For computational use, the concentration profile should either be scaled or constrained so as not to exceed the chemical density as an upper limit.

The far field equations are also constrained or limited to distances $x > x_c$ at which the condition of uniform cross-channel mixing can be assumed.

(d) Maximum Hazard Extent

The steady state equation gives the maximum concentration reached at a location x for a continuous discharge which emits indefinitely. For a discharge of finite duration, the steady state equation gives an upper limit which can be very approximately used to estimate the maximum concentration at any location x, and has the advantage that the simple form of the equation is readily inverted to express a maximum hazard extent, x, in terms of a specified hazardous concentration C_H:

$$x = \frac{2E}{\Omega - u} \ln\left(\frac{\dot{M}}{C_H A \Omega}\right) \tag{549}$$

or

$$x = \frac{u}{k} \ln\left(\frac{\dot{M}}{C_H A u}\right) \qquad \text{if } E \ll \frac{u^2}{4k} \tag{550}$$

For the special case of no decay, k=0, the steady state concentration distribution reduces to a constant

$$c(x) = \frac{\dot{M}}{Au} \quad , \; k=0 \tag{551}$$

and thus inversion to obtain a coordinate for a specified hazard level is inappropriate.

(e) Arrival Time and Duration

With the far field equation, as the chemical is dispersed downstream, the concentrations in downstream water increase with time until the steady state value is reached, for a discharge which emits continuously. As the chemical moves downstream, a relationship exists between elapsed time and downstream distance in the form:

$$x = \Omega t \pm n\sqrt{4Et} \tag{552}$$

where n is taken as an integer value greater than 1. In particular, at a given downstream location x, a rise in concentration will not be appreciable until time increases beyond a value that satisfies the equation:

$$x = \Omega t + n\sqrt{4Et} \tag{553}$$

As an approximate guide for use in scaling concentration profiles, the earliest time of arrival at a given location x can be estimated from $t = \frac{x}{\Omega}$. For continuous discharges which stop after a duration t_{mt}, the duration of the concentration history at an observation point x is also t_{mt} and the maximum elapsed time of interest is then very approximately $\frac{x}{\Omega} + t_{mt}$.

(2) $t > t_{mt}$

When the observation time t is greater than the duration of the continuous release, the upper limit of the original integral expression for the concentration, τ_s, is equal to the duration of the discharge, t_{mt}.

Substitution of this limit in the general form of the concentration equation directly leads to the result:

$$c(x,t) = \frac{\dot{M}}{2A\Omega} e^{\frac{xu}{2E}} \left\{ e^{\frac{\Omega x}{2E}} \left[\text{erf}\left(\frac{x+\Omega t}{\sqrt{4Et}}\right) - \text{erf}\left(\frac{x+\Omega(t-t_{mt})}{\sqrt{4E(t-t_{mt})}}\right)\right] - e^{-\frac{\Omega x}{2E}} \left[\text{erf}\left(\frac{x-\Omega t}{\sqrt{4Et}}\right) - \text{erf}\left(\frac{x-\Omega(t-t_{mt})}{\sqrt{4E(t-t_{mt})}}\right)\right]\right\} \tag{554}$$

As the elapsed time t becomes very large with respect to the duration of the release t_{mt}, the error function terms cancel, and analytically the concentration vanishes. However, the same type of instability in products of exponential and error function terms occurs. Also, caution must be used in evaluating the error function terms for t approximately equal to t_{mt} due to the appearance of the term $t-t_{mt}$ in the denominator.

SECTION V

MODELS FOR ESTUARIES AND TIDAL RIVERS

1. INTRODUCTION

In Section IV, the dispersion of a spilled chemical into a non-tidal river was shown to be conceptually similar to a spill into still water, subject mainly to the influence of two additional factors introduced by the flowing river: the bulk fluid motion of the river current and the constraints imposed by the banks and bottom of the river channel. Similarly, the dispersion of a spilled chemical into a tidal river or estuary is analogous to the behavior of a spill into a non-tidal river, subject to the additional influence of the oscillatory behavior of the bulk fluid flow, and the effect of salinity intrusion.

Models for two types of water bodies are considered. The constant density regions of an estuary where salinity intrusion is minimal are designated as tidal rivers. In these regions the spill behavior is subject only to the single additional influence of the oscillatory bulk fluid flow. For tidal rivers, the river system coordinates and channel geometry are the same as those for a non-tidal river as identified in Section I. On the other hand, estuaries designate saline regions where both tidal action and the density gradiant driven circulation are significant.

The behavior of a dispersing chemical will be influenced in addition by variations in the velocity distribution, wave and wind generated turbulence, channel irregularities and other factors. After a spill, the size of the dispersing mass increases, passing through different stages from an initial three-dimensional distribution to eventually a more or less uniform distribution across the channel cross-section. In non-tidal rivers, resulting from width to depth ratios commonly much greater than one, an intermediate stage of dispersion is usually reached based on the assumption of uniform dispersion across the depth of the river channel. However, in regions of salinity intrusion, density stratification effects may instead cause uniform spreading across the width of the channel to occur first. In practical application, the differences in possible local effects in the immediate vicinity of the spill location, and the difficulty of determining reliable estimates of the diffusion coefficients e_x, e_y, and e_z for three- or even two-dimensional spreading restrict the development of these generalized models to one-dimensional behavior. Except for regions very close to the spill, use of concentrations obtained as cross-sectional averages appears adequate for the types of situations of interest and one-dimensional models are assumed.

a. Tidal Velocity

In tidal rivers and estuaries, the tidal component of the bulk water body fluid motion is superimposed on a non-tidal fresh water component. While in non-tidal rivers, the bulk transport of a spilled chemical occurs in only one direction, the oscillatory bulk fluid movement of tidal rivers and estuaries contributes to movement both downstream and upstream.

The velocity of water in tidal rivers is dependent on the non-tidal rate of discharge of the water in the river and the superimposed effect of the rising and falling tides. The non-tidal component of the water velocity is denoted by u_f, and is the same as the velocity used for the non-tidal river. This outflow stream velocity can be estimated by determining the stream velocity of the river at an upstream location which is not affected by tidal action. Alternatively it can be estimated from the Tidal Current Tables by subtracting the maximum flood current velocity from the maximum ebb current velocity.

The amplitude of the superimposed sinusoidal tidal flow velocity is denoted by u_t, and values can be obtained for the region of concern by referring to the Tidal Current Tables for the region and computing the average of the maximum ebb and flood current velocities. The units of measure of u_t are the same as for u_f.

Since the superimposed tidal flow velocity, u_t, of a tidal river is both along the direction of flow velocity of a river, u_f, during falling tide and opposite to the direction of the flow of the river during rising ride, the total flow velocity of a tidal river denoted by u(t), can be represented by:

$$u(t) = u_f + u_t \sin \{\sigma \ (t-\delta)\} \tag{555}$$

where t is elapsed time from the start of the spill, and δ is the phase lag or time to the next highwater slack tide (high tide). The value of the phase lag might range from 0 to 12 or more hours.

Denoting the tidal period, the time period from one high tide to the next or from one low tide to the next, by t_p, the value of σ in the above is obtained as:

$$\sigma = \frac{2\pi}{t_p} \tag{556}$$

and the tidal river velocity representation becomes:

$$u(t) = u_f + u_t \sin\left\{ \frac{2\pi}{t_p} (t-\delta)\right\} \tag{557}$$

where the river velocity u(t) is a function of time. Depending on the relative magnitudes of u_f and u_t, the river velocity u(t) will change in magnitude over time, and may also change in sign if $u_t > u_f$ representing movement both downstream and upstream.

b. Types of Models

From Section IV.2.c, the form of the diffusion equation assumed to govern the distribution in a tidal river or estuary is given by:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = \frac{1}{A} \frac{\partial}{\partial x} \left(E\ A \frac{\partial c}{\partial x} \right) - kc \tag{558}$$

where the concentration c is a function of downstream distance from the spill location, x, and time t, and gives the average concentration over the cross section of the river channel. Since a cross-sectional average is obtained, this result is independent of the relative spill location (offset) across the channel width.

As with non-tidal rivers, the dispersion coefficient e_x has been replaced by an effective longitudinal dispersion coefficient E which represents not only the dispersion represented by e_x but also the dispersion of the chemical due to the differential velocities and concentrations across the channel. In the above form of the dispersion equation, the longitudinal dispersion coefficient may be taken to be a function of both time and distance: E(x,t).

Most existing tidal river models are one-dimensional and in general these include tidally averaged models and intratidal or real-time models. The tidally averaged models are useful only when the dispersion time is much greater than the tidal period, and treat the tidal oscillations as part of the large scale longitudinal dispersion. This leads to using a constant outflow velocity u_f; the governing concentration equation is the same as for a non-tidal river with the exception that tidally averaged longitudinal dispersion coefficients are used.

Intratidal or real time models treat the tidal flow to be advective, with longitudinal dispersion having time scales that are much shorter than a tidal cycle. Hence, the tidal river velocity is assumed as a function of time u(t) and concentration equations are obtained as solutions of the above partial differential equation.

2. MODELS FOR ESTUARIES

a. Introduction

Estuaries differ from rivers and natural streams because of oscillatory tidal advection and gradient induced circulation due to salinity differences. Except for the lower reaches of an estuary, one dimensional models adequately estimate dispersion by averaging over the cross-sectional area. The form of the differential equation governing the mixing and dilution of the pollutant is obtained from:

$$\frac{\partial c}{\partial t} + u(t)\,\frac{\partial c}{\partial x} = \frac{1}{A(x,t)}\,\frac{\partial}{\partial x}\left\{A(x,t)\;E(x,t)\,\frac{\partial c}{\partial x}\right\} - kc \qquad (559)$$

and this can be re-written as:

$$A(x,t)\frac{\partial c}{\partial t}+Q(x,t)\frac{\partial c}{\partial x}=\frac{\partial}{\partial x}\left\{A(x,t)\ E(x,t)\frac{\partial c}{\partial x}\right\}-k\ A(x,t)\ c \qquad (560)$$

where

c is the concentration as a function of time t and distance x,

A(x,t) is the cross-section area,

Q(x,t) is the discharge,

E(x,t) is the sectionally averaged one dimensional longitudinal dispersion coefficient, and

k is the chemical decay rate constant

To obtain estimates of the pollutant concentration, it is assumed for the above formulation that data describing A(x,t) and Q(x,t) are available, in addition to the dispersion coefficient E. The solution for c(x,t) is then obtained for the specific initial and boundary conditions. For simplification, concentrations can be obtained using either a tidally averaged approximation or an intratidal approximation. Tidally averaged models are the simplest and involve treating the tidal oscillations as part of the large scale longitudinal diffusion. Intratidal models treat the tidal flow to be advective, with longitudinal diffusion having time scales that are much shorter than a tidal cycle.

b. Tidally Averaged Model

The tidally averaged model is obtained in the same form as the one-dimensional river or natural stream model. The governing differential equation is obtained as:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = E \frac{\partial^2 c}{\partial x^2} - kc \qquad (561)$$

where

c is the time and sectionally averaged concentration,

u is the constant fresh water velocity, and

E is the longitudinal dispersion coefficient

Solutions of this equation are obtained in the form:

$$c(x,t) = \frac{M}{A\sqrt{4\pi Et}} e^{-\frac{(x-ut)^2}{4Et}} e^{-kt} \qquad (562)$$

where M is the amount of chemical assumed to be discharged instantaneously. The form of this equation is the same as that obtained for the far field approximation of a spill into a non-tidal river.

In order to evaluate the longitudinal dispersion coefficient E, Hetling and O'Connell[57] found in their studies on the Potomac River that the following empirical equation could be used:

$$E = 1680.\ u_0^{4/3} \qquad (563)$$

where

E is the sectionally and tidally averaged one dimensional longitudinal dispersion coefficient, and,

u_0 is the maximum tidal velocity (in knots)

This equation is appropriate for calculations that are allowed to vary within one order of magnitude, and is expected to generally produce conservative results. Experimental data, if available, could instead be substituted directly into the concentration equation.

c. Intratidal Model

Considering the tidal flow to be advective, with longitudinal dispersion having a time scale much shorter than a tidal cycle, leads to the following form of the diffusion equation:

$$\bar{Q}(x) \frac{\partial \bar{c}}{\partial x} = \frac{\partial}{\partial x} \left\{ \bar{A}(x) \; \bar{E}(x) \frac{\partial \bar{c}}{\partial x} \right\} - k \; \bar{A}(x) \; \bar{c} \qquad (564)$$

where the averaged concentration $\bar{c}$ depends upon

$\bar{Q}(x)$, the time averaged discharge

$\bar{A}(x)$, the tidally averaged flow area, and,

$\bar{E}(x)$, the time averaged longitudinal dispersion coefficient

Thatcher and Harleman[58] have found that the longitudinal dispersion coefficient can be approximated using the correlation:

$$\frac{K}{u_0 L} = f \; (E_D) \qquad (565)$$

where

u_0 = maximum flood velocity at the entrance to the estuary,

L = length of the salinity intrusion region of the estuary,

K = dispersion parameter, and,

E_D = estuary stratification parameter

The dispersion parameter K can be approximated by:

$$K = 0.00215 \; u_0 \; L \; E_D^{-0.25} \qquad (566)$$

The estuary stratification parameter or estuary number can be approximated by:

$$E_D = \frac{P_T F_D^2}{Q_f t_p} \qquad (567)$$

where

P_T = volume of water entering the estuary in flood tide (tidal prism)

Q_f = fresh water discharge, volume/time

t_p = tidal period, and

F_D = densimetric Froude number at the entrance to the estuary, obtained as a function of the change in density over the entire length of the estuary

The correlation leads to an approximation for the longitudinal dispersion coefficient:

$$\bar{E} = K \left| \frac{\partial \overset{\circ}{s}}{\partial \overset{\circ}{x}} \right| + 77 \; n \; u \; R_h^{5/6} \qquad (568)$$

where K is defined above and:

$\overset{\circ}{s}$ = dimensionless one-dimensional salinity gradient, $\frac{s}{s_0}$

s = local salinity

s_0 = salinity at mouth

$\overset{\circ}{x}$ = dimensionless ratio of distance from mouth (x) to length of estuary (L)

n = Manning roughness factor

u = average velocity, and,

R_h = hydraulic radius

Since the variables in this formulation are specific to the individual estuary, each situation and locale provides a unique environment that must be evaluated separately and a generalized solution of the differential equation can not be obtained without recourse to numerical methods. In addition, the requirement for extensive site specific data to obtain estimates of the longitudinal dispersion coefficient restricts the application of these equations for general use under emergency spill conditions.

3. MODELS FOR TIDAL RIVERS

a. Introduction

For spills into the constant density regions of an estuary, designated as tidal rivers and where salinity intrusion is minimal, the differential equation governing the mixing and dilution of the pollutant is given by:

$$\frac{\partial c}{\partial t} + u(t)\frac{\partial c}{\partial x} = \frac{1}{A(x,t)}\frac{\partial}{\partial x}\left\{A(x,t)\;E(x,t)\;\frac{\partial c}{\partial x}\right\} - kc \qquad (569)$$

where the velocity of the water in the tidal region, u(t), is assumed to have a sinusoidal variation, as described in Section V.1.a, and the concentration c is obtained as a function of x and t. Since this is a one-dimensional equation, the results obtained are based on the assumption of a uniform distribution of the pollutant concentration throughout the cross-section of the river. Thus the concentrations will only be approximately correct for elapsed times sufficiently long after the start of the spill for uniform cross-sectional mixing to have occurred.

For practical application in a generalized model intended for use in different environmental settings under emergency conditions, it is not possible to obtain descriptions of the channel geometry, A(x,t), and the longitudinal dispersion coefficient, E(x,t), as functions of time and distance. Assuming constant average values, the governing differential equation for the tidal river model becomes:

$$\frac{\partial c}{\partial t} + u(t)\,\frac{\partial c}{\partial x} = E\,\frac{\partial^2 c}{\partial x^2} - kc \tag{570}$$

The river system coordinates and channel geometry (d = depth, w = width) are taken to be the same as for a non-tidal river (Section I.4.a). Chemical decay or degradation on release is denoted by the decay constant k.

Two tidal river sub-models are considered in the following sections depending on the type of release: instantaneous or continuous. The instantaneous model is obtained as a solution of the above differential equation. The continuous release model is obtained, using the principle of superposition, by integrating the concentration equation for an instantaneous release.

b. Instantaneous Spill Model

Except for the sinusoidal variation of the bulk motion of the receiving water body, the differential equation for the concentration distribution in a tidal river has the same form as the equation for a discharge into a non-tidal river. For the non-tidal river, the solution for an instantaneous release is obtained as a Gaussian distribution, the center of mass of which is translated downstream at a rate equal to the constant river velocity u. This is equivalent to a coordinate translation in the downstream direction of x-ut.

For the case of a spill into a tidal river then the concentration distribution is obtained as a Gaussian distribution, written in general form as:

$$c(x,t) = \frac{a}{\sqrt{E(t-\tau)}} \, e^{-\frac{b[x-f(t-\tau)]^2}{E(t-\tau)}} \cdot e^{-k(t-\tau)} \qquad (571)$$

where

$c(x,t)$ gives the concentration at a location x and time t,

τ gives the time the discharge occurs,

$t-\tau$ gives the elapsed time from the start of the discharge,

a,b are constants to be determined, and

$f(t-\tau)$ is a function of the sinusoidal river velocity governing the bulk motion of the dispersing mass

Usually this equation is written for t representing elapsed time from the start of the discharge so that the term τ does not appear (i.e., is equal to zero). This form of the equation is more convenient however for expressing the integrand to obtain solutions for continuous releases.

For an instantaneous discharge occurring at time τ, the concentration is given by the above equation for $t > \tau$ and $c(x,t) = 0$ for $t < \tau$.

(1) Determination of Constants

(a) Use of Governing Equation

Substitution of the general form of the concentration equation into the governing partial differential equation leads to the following result:

$$\frac{c(x,t)}{(t-\tau)^2} \left\{ (1-4b) \left[\frac{b(x-f(t-\tau))^2}{E} - \frac{(t-\tau)}{2} \right] + \frac{2b(t-\tau)}{E} (x-f(t-\tau)) \cdot \left(\frac{df(t-\tau)}{dt} - u(t) \right) \right\} = 0 \qquad (572)$$

Since this must hold for all values of x and t, as $t \rightarrow \tau$, the term in brackets reduces to:

$$(1-4b) \cdot \frac{b}{E} \cdot \left(x-f(0) \right)^2 = 0 \qquad (573)$$

For the equality to hold for any value of x, the constant b in the concentration equation is obtained as $b = \frac{1}{4}$. Using this value, the above equation reduces to:

$$\frac{c(x,t)}{2E(t-\tau)} \cdot \left\{ x-f(t-\tau) \right\} \cdot \left\{ \frac{df(t-\tau)}{dt} - u(t) \right\} = 0 \tag{574}$$

At any time $t > \tau$, for any value of x, this equation is satisfied for:

$$f(t-\tau) = \int_{\tau}^{t} u(\xi)\, d\xi \tag{575}$$

(b) Conservation of Mass

The second constant in the concentration equation is determined from conservation of mass where the integral of the concentration over the volume of the water body is equal to the total quantity of substance in the environment. Because both the concentration and the total mass are related in the same manner to the exponential decay term, this term can be ignored and conservation of mass stated in terms of a conservative pollutant: the total mass dispersing in the water body at any time t is equal to the total mass initially spilled, M. This gives the equation:

$$M = \iiint c(x,t)\, dx\, dy\, dz = \int_{-\infty}^{\infty} c(x,t)\, dx \cdot \iint dy\, dz \tag{576}$$

The integral over the dimensions of the water body in the y and z directions is simply the cross-sectional area of the river channel and is denoted by A. Substituting the general form of the concentration equation then gives:

$$M = A \int_{-\infty}^{\infty} \frac{a}{\sqrt{E(t-\tau)}}\, e^{-\frac{b[x-f(t-\tau)]^2}{E(t-\tau)}}\, dx \tag{577}$$

where the exponential decay term is ignored. The integral is evaluated using the definition of the error function to obtain:

$$M = \frac{A \cdot a}{\sqrt{b}} \int_{-\infty}^{\infty} e^{-\xi^2} \, d\xi = \frac{A \cdot a}{\sqrt{b}} \cdot \sqrt{\pi} \tag{578}$$

Substituting $b = \frac{1}{4}$ and solving for the constant a gives:

$$a = \frac{M}{2A\sqrt{\pi}} \tag{579}$$

(c) Summary

Substituting the values for the constants a, and b, in the concentration equation gives the resulting equation for an instantaneous spill in the form:

$$c(x,t) = \frac{M}{2A\sqrt{\pi}\sqrt{E(t-\tau)}} e^{-\frac{[x-f(t-\tau)]^2}{4E(t-\tau)}} \cdot e^{-k(t-\tau)} \tag{580}$$

where

$$f(t-\tau) = \int_{\tau}^{t} u(\xi) \, d\xi \tag{581}$$

and the sinusoidal velocity of the tidal river is given by:

$$u(\xi) = u_f + u_t \sin\left\{ \frac{2\pi}{t_p} (\xi-\delta) \right\} \tag{582}$$

Evaluating the integral expression for f(t-τ) gives:

$$f(t-\tau) = u_f(t-\tau) - \frac{u_t t_p}{2\pi}\left[\cos\left\{\frac{2\pi}{t_p}(t-\delta)\right\} - \cos\left\{\frac{2\pi}{t_p}(\tau-\delta)\right\}\right] \quad (583)$$

For use only with an instantaneous spill, the formulation of the above expressions can be simplified somewhat by taking $\tau = 0$ to obtain:

$$c(x,t) = \frac{M}{2A\sqrt{\pi}\sqrt{Et}} \cdot e^{-\frac{[x-f(t)]^2}{4Et}} \cdot e^{-kt} \quad (584)$$

$$f(t) = u_f t - \frac{u_t t_p}{2\pi}\left[\cos\left\{\frac{2\pi}{t_p}(t-\delta)\right\} - \cos\left\{\frac{2\pi\delta}{t_p}\right\}\right] \quad (585)$$

where t is taken as elapsed time from the instantaneous discharge. The instantaneous equations are used with $\tau > 0$ however to develop the concentration equation for a continuous discharge. The location of the spill is taken as x=0. Note that for times $t < \tau$, the concentration $c(x,t) = 0$.

(2) Determination of Longitudinal Dispersion Coefficient

The method of computing the longitudinal dispersion coefficient, E, is obtained from reference[12], and gives reasonably accurate values for well defined straight channels. The results are not applicable to multi-channeled or island-studded estuaries. It is also assumed that the non-tidal water body velocity component, u_f, is much smaller than the tidal component, u_t.

First, effective transverse and vertical dispersion coefficients are defined as:

$$E_v = 6\ d\ U^* \tag{586}$$

where

E_v = dispersion coefficient predominently affected by vertical velocity gradients in m^2/second

d = river depth in meters

U^* = shear velocity in meters/second

and

$$E_t = 0.011 \left(\frac{u_t t_p}{b} \right)^2 \left[\frac{\overline{u''}^2}{\left(\frac{2}{\pi} u_t \right)^2} \right] E_v \tag{587}$$

where

E_t = dispersion coefficient primarily influenced by transverse velocity variation in m^2/second

u_t = amplitude of tidal velocity in m/second

$\overline{u''}$ = velocity deviation from uniform conditions

t_p = tidal period in seconds

b = half width (w/2) of the river in meters

The term in brackets is reported as ranging from 0.01 to 0.04; the mean value of 0.025 is used to give:

$$E_t = (0.011)\ (0.025) \left(\frac{u_t t_p}{b} \right)^2 E_v \tag{588}$$

The value of the longitudinal dispersion coefficient E is taken as either E_t or E_v. To determine which of the two dispersion coefficients to use, two characteristic time ratios are defined:

$$T_v = \frac{t_p}{d^2/e_z} \tag{589}$$

where

T_v = diffusional time ratio for vertical spreading

t_p = tidal period in seconds

d = river depth in meters

e_z = vertical turbulent dispersion coefficient in m^2/second

and

$$T_t = \frac{t_p}{b^2/e_y} \tag{590}$$

where

T_t = diffusional time ratio for transverse spreading

b = half-width (w/2) of river in meters

e_y = transverse turbulent dispersion coefficient in m^2/second

If $T_v < 1$, then the dispersion coefficient E is given by E_v. If $T_v > 1$ (and $T_t < 0.1$), then E_t is calculated, and if $E_t > E_v$ then $E = E_t$. Otherwise $E = E_v$.

It should be noted that for $T_v > 1$, the coefficient E is taken as the largest of E_t or E_v, and that the ratio E_t/E_v may be very large. Reference[12] indicates that a maximum value of about 11 for E_t/E_v has been reported for several estuaries.

(a) Shear Velocity

The shear velocity, U^*, for the non-tidal river case was given as:

$$U^* = \sqrt{\tau_0/\rho} = 3.115\ n\ u/R_h^{1/6},\ \text{m/second} \tag{591}$$

where

τ_0 = wall shear stress

ρ = density of fluid

n = Manning roughness factor

R_h = hydraulic radius

u = average velocity of cross section for the non-tidal river

For use with the tidal river case, the velocity term is replaced by the mean oscillating flow velocity. The oscillating river velocity is given as a function of time by:

$$u(t) = u_f + u_t \sin \frac{2\pi}{t_p} (t-\delta) \tag{592}$$

The mean oscillating flow velocity, denoted by u_m, is obtained by integrating the oscillating velocity component over one-half the tidal period:

$$u_m \frac{t_p}{2} = \int_{\delta}^{\delta + \frac{t_p}{2}} u_t \sin \frac{2\pi}{t_p} (t-\delta)\, dt \qquad (593)$$

Evaluating the integral gives:

$$u_m \frac{t_p}{2} = \frac{u_t}{\pi} \frac{t_p}{2} \int_0^{\pi} \sin \Theta \, d\Theta = \frac{u_t t_p}{\pi} \qquad (594)$$

The mean oscillating flow velocity, u_m, is then obtained as:

$$u_m = \frac{2\ u_t}{\pi} \qquad (595)$$

Substituting this expression then gives the equation for the shear velocity in the form for use with the tidal river model as:

$$U^* = 3.115\ n \left(\frac{2\ u_t}{\pi} \right) R_h^{-1/6}, \text{ m/second} \qquad (596)$$

The equation for the hydraulic radius is obtained from the non-tidal river model section, and is given by:

$$R_h = \frac{w \cdot d}{2d+w} \qquad (597)$$

Values of the Manning roughness coefficient are tabulated in the non-tidal river model section.

(b) Turbulent Dispersion Coefficients

The computation of the characteristic time ratios, T_v and T_t, requires the values of the vertical and transverse turbulent dispersion coefficients, e_z and e_y, respectively. The equations for these coefficients are the same as given for a non-tidal river, that is:

$$e_z = 0.067\ U^* R_h \tag{598}$$

and

$$e_y = 0.1\ e_z \text{ if } \frac{w}{d} > 100 \tag{599}$$

or

$$e_y = 0.23\ U^* R_h \text{ if } \frac{w}{d} < 100 \tag{600}$$

where e_y and e_z are in m^2/second. Since the formulation of the shear velocity differs, the actual values of e_y and e_z will differ from the non-tidal river case even though the same equations are used.

(c) Limitations

The formulation of the expressions for the longitudinal dispersion coefficient E is based on the assumption that $u_f << u_t$. Also, the selection of the dispersion coefficient based on the values of characteristic diffusional time ratios examines only values normally expected for most tidal channels, and the diffusional time ratio for transverse spreading is not utilized.

c. Continuous Spill Model

A continuous discharge is assumed to occur at a rate $\dot{M}(t)$ over a period of time from $t=0$ to $t=t_{mt}$ at which time the discharge stops. The concentration produced by an incremental discharge, occurring at time τ, is given as a function of time by the instantaneous equation:

$$\Delta c(x,t) = \frac{\dot{M}(\tau)\, d\tau}{2A\sqrt{\pi}\sqrt{E(t-\tau)}}\, e^{-\frac{[x-f(t-\tau)]^2}{4E(t-\tau)}}\, e^{-k(t-\tau)} \tag{601}$$

where $c(x,t)$ is taken as zero for $t < \tau$. The complete concentration distribution produced by the continuous discharge is obtained by summing or integrating the contributions from each of the incremental instantaneous releases. Since the release is assumed to be of finite duration, this gives two cases of interest: $t < t_{mt}$ and $t > t_{mt}$.

(1) $t < t_{mt}$

When the observation time is less than the duration of the release, the incremental instantaneous discharges are integrated over $\tau = 0$ to $\tau = t$ to obtain the expression for concentration from a continuous discharge which starts at time $t = 0$:

$$c(x,t) = \int_0^t \frac{\dot{M}(\tau)}{2A\sqrt{\pi}\sqrt{E(t-\tau)}}\, e^{-\frac{[x-f(t-\tau)]^2}{4E(t-\tau)}}\, e^{-k(t-\tau)}\, d\tau \tag{602}$$

for $t > \tau$. The integrand is taken to be zero for $t < \tau$ and $t < 0$. The spill rate $\dot{M}(\tau)$ appears in the integrand as a function of time, and in general a variable rate could be used if the integral is evaluated numerically. For practical application however a constant rate of release is assumed.

The exponential term, $f(t-\tau)$, is obtained from the general equation for the instantaneous release as:

$$f(t-\tau) = u_f(t-\tau) - \frac{u_t t_p}{2\pi} \left[\cos\left\{\frac{2\pi}{t_p}(t-\delta)\right\} - \cos\left\{\frac{2\pi}{t_p}(\tau-\delta)\right\} \right] \quad (603)$$

(2) $t > t_{mt}$

When the observation time is greater than the duration of the continuous release, the resulting concentrations at time t are obtained by integration of the instantaneous distribution for releases from $\tau = 0$ to $\tau = t_{mt}$. The expression for the integrand does not change.

The spill model uses a numerical integration algorithm to determine the value of either of these integrals for selected values of x and t.

SECTION VI

REVIEW OF MAJOR ASSUMPTIONS

Because of the complexity of the chemical spill process, the uncertainties and variabilities associated with spill conditions and the nature of the environment in the vicinity of the spill, and the difficulties inherent in describing these phenomena, the analysis and implementation of the water dispersion model have necessarily been based on numerous assumptions. The degree of sophistication that has been attempted has been carefully considered, and assumptions or limitations introduced to enable the models to be applied to a class of non-chemical specific discharges in a range of environmental settings. Also, these models are intended for use in real or threatened emergency spill situations, in addition to routine assessments for contingency planning, and thus the input data required is restricted to that information that can be readily observed, estimated, or assumed from on-scene observations or reports; use of extensive, detailed site specific data is precluded.

Major assumptions and/or limitations that are incorporated in the model have been discussed in the text and are summarized for review in the following paragraphs.

Heat sources and heat sinks are neglected, and the assumption is made that the initial temperature of the spilled chemical and the receiving water body are nearly equal. Any initial unequal temperatures would ultimately come to equilibrium at a temperature very nearly equal to the temperature of the water into which the spill occurs because of the comparatively large thermal capacity of a river, lake, or ocean into which a spill may occur.

During the initial stages of dispersion, the difference in the temperatures of the spilled chemical and the receiving water could affect the rate of dispersion. The significance of this assumption depends on the type of chemical and relative temperature ranges at which these are transported.

Temperature differences may also give rise to buoyancy effects. Studies of these effects have been reported in the literature, many of which deal with thermal discharges from power plants or waste water discharges through submerged outlets or distributed outfalls. In these cases, the discharge is lighter than the receiving water. The movement of the discharge as it rises creates secondary induced turbulent currents, and the rate of dispersion and manner in which it takes place are effected. The water dispersion model described in this report assumes that the spill occurs onto the surface of the waterway, and the effect of buoyancy has not been incorporated. Thus the model strictly is most appropriate for those liquids that are neither significantly lighter nor denser than the receiving water. The model may also be applied for the dispersion of solid particles, if these are neutrally buoyant or if the settling times are large in comparison to the dispersion.

Chemical degradation in the aquatic environment has been modeled by a first order rate constant process. Additional effects of chemical reactions or phase changes during dispersion have not been incorporated. Phenomena associated with chemical reactions which were neglected include resulting dispersion of the products of reaction and thermal effects from the heat of reaction. The most significant model assumption may be that no vapor is liberated, and that, other than a first order decay, the entire mass of spilled chemical is dispersed. The model assumes the chemical is fully soluble in water (miscible in all proportions) and that all the discharged chemical goes into solution with water. A separate model was developed for use in HACS to estimate vaporization rates; however, the resulting reduction of the mass dispersing in water has not been incorporated. This assumption leads to estimates of concentrations in water that are conservative.

Stratification of the receiving water body and the interaction with density or buoyancy effects have not been included, although the receiving water body is considered to be non-isotropic, with different but constant dispersion coefficients along each axis. Thermal layers in lakes and oceans are known to exist at some depths, at some or all different times of the year, depending on seasonal temperature variations. These horizontal layers, when present, can act as confining boundaries by significantly inhibiting dispersion to greater depths, reflecting the dispersing chemical and limiting mixing to occur in the upper portion of the water body. Modification of the still water model to incorporate confining boundaries, using the method of imaging or virtual sources, would not present significant difficulty, provided that depths to these boundaries could be estimated.

Strictly, the models apply to spills of large quantities that occur under assumed instantaneous or continuous discharge conditions. For continuous discharges, the rate at which the chemical is released is assumed to be constant. An analysis of the continuous release model has formulated an approach in which a variable mass release rate can be modeled. However, as implemented, the model is limited to a constant release rate since for the purpose of expected use it was assumed that inadequate information would be available to accurately characterize a variable rate.

River channels are modeled as having a constant rectangular cross-section, and for non-tidal rivers, a constant cross-sectional average river velocity has been assumed. For tidal rivers, the tidal effect has been modeled by a sinusoidal velocity imposed on the non-tidal component. Velocity variations caused by winds, storms, local channel obstructions, and similar effects have not been included. The boundaries (banks and channel bottom) of the river channel have been assumed to be impenetrable to the dispersing mass, and only first-order image sources have been included to model the effect of confined dispersion.

In regions near to the source for a continuous discharge into a river, the additional longitudinal travel due to longitudinal dispersion is neglected with respect to the bulk motion of the dispersing mass in the direction of river travel. This assumption is strictly applicable to rivers in which the rate of longitudinal diffusion is small with respect to the movement with the river velocity; however, all but the most slowly flowing rivers will give reasonably good agreement with this assumption.

At distances far from the location of a spill into a non-tidal river, a simplifying assumption is made that the dispersing mass reaches a uniform cross-sectional distribution, and further dispersion occurs in a one-dimensional manner in the direction of river flow. While the assumption is reasonably consistent with the expected behavior of the mass at large distances from the spill, and introduces some simplicity in the model formulation, the resulting difference in the modeling equations may cause a discontinuity in concentration estimates between the near and far regions. Since the model incorporates, to a first order, the boundary effects in the region near the spill site, concentrations reached at long distances from the spill location should be expected to approximate those obtained by one-dimensional analysis, and as a result the one-dimensional analysis is not essential. The model does not currently include provision for automatically forcing a match between these near- and far-field equations, and the results obtained should instead *be interpreted in terms of the type of dispersion being modeled.*

Although some of these assumptions and limitations have greater effect than others, it is generally concluded that the assumptions lead to a simplified, but reasonably realistic, model with which estimates of concentration distributions can be obtained on the same order of accuracy as the accuracy to which the required model inputs are available.

SECTION VII

SENSITIVITY ANALYSES

Extended sensitivity analyses could not be conducted within the time available for this project, and the discussion that follows is based on the results of previous studies [12], [20]. Since these studies utilized earlier versions of the water dispersion model, the observations reported here should be considered as preliminary. Also, sensitivity analyses generally utilize perturbations of selected variables about a set of nominal values for all independent and dependent variables. Because of the complexity of the models and the effects of different combinations of independent variables, different behavior can be observed about different sets of nominal values. A more effective approach to determining the relative effects of different independent variables on the resulting concentrations is to assess the behavior of the analytical formulation of the model, as has been done in the body of this report, identifying the regions of different behavior and describing the manner in which independent variables affect limit conditions.

The concentration distribution obtained in water is primarily a function of a spatial position, time, geometry of the water region, spill mass or discharge rate, river channel roughness, characteristics of the transporting fluid flow (non-tidal velocity, tidal period, phase lag and amplitude), and decay coefficient. The concentration predicted is directly proportional to the quantity of mass spilled (or rate of mass spill); that is, a 1 percent change in mass spilled causes a 1 percent change in concentration. The dependence of the maximum concentration on the velocity and the geometry is more complicated.

In the case of a river (non-tidal), the maximum concentration predicted, close to the spill point, at a particular instant is inversely proportional to the square root of the velocity cubed; that is, a 1 percent change in the velocity causes a 1.5 percent change in concentration. For tidal rivers, approximately the same results also hold. However, the velocity considered should be the tidal velocity instead of the stream velocity.

The dependence of the concentration on the geometry is very complicated. The rougher the surface of the channel, the greater is the turbulence and the smaller the concentration. The concentration is also inversely proportional to the cross-sectional area for large distances from the point of spill. For shallow rivers, the near-field concentration varies as $(\text{depth})^{1.25}$; that is, for a 1 percent change in depth, the change in concentration is -1.25 percent. The far-field concentration varies inversely with depth; that is, for a 1 percent change in depth, -1 percent change in the concentration results, with the other parameters remaining the same.

Chemical degradation in the aquatic environment is incorporated using exponential decay factors, e^{-kt}, and depending on the value of the rate constant and the range over which kt is small (such that $e^{-kt} \sim 1$) or large, the effect on the resulting concentrations will either be negligible or significant. Increasing the decay coefficient decreases the concentration of the dispersing mass.

For discharges into rivers, the location of the center of the dispersing chemical mass, and hence, the point of maximum concentration, is directly dependent on the river velocity. Also, an increase in the river velocity causes the turbulence level to increase with a consequent increase in the shear velocity. For one-dimension dispersion, this increases the dispersion coefficient which, in turn, causes a corresponding concentration decrease.

Water temperature and also possibly river channel roughness, when compared to other variables, appear to have only minimal effect on concentration for the particular model assumptions and limitations (e.g., neutral buoyancy).

The river depth and width affect the concentration of a dispersing mass in a manner such that the greater the depth or width, the smaller the turbulence level in the river, and when the turbulence level in the river is small, the shear velocity is also small. However, at the same time increasing either the depth or width increases the hydraulic radius of the river, so that the effect of these changes on values of dispersion coefficients computed as a function of the product of the shear velocity and hydraulic radius would be to either increase or decrease the coefficient values.

As demonstrated by example for conservation of mass, expressions of the form $\sqrt{e_x t}$ indicate the degree of spreading in the particular coordinate direction from the center of the dispersing mass. The spreading of the dispersing mass will occur more rapidly in directions of larger dispersion coefficients; this spreading will cause concentrations to be reduced more rapidly in these directions but also accompanied by a more rapid movement to greater distances. It is also noted that differences in the method of computation of dispersion coefficients, for different river width-to-depth ratios, or for one-dimensional or three-dimensional spreading, will, in general, cause concentration discontinuities at the transition.

Since the maximum concentration is obtained at the spill location in still water, or at the initial origin of the spill translated by a distance determined by the bulk velocity of fluid flow, the relationship between this point and a point chosen for observations will significantly affect the concentrations obtained at the observation point. Increased concentrations will occur as the observation point is taken at distances closer to the center of the dispersing mass. At observation points removed from the center of this mass, concentrations will increase with increases in elapsed time until a certain time at which the concentration at the observation point reaches a maximum. After that time, further increases in time will result in decreasing concentrations. The maximum concentration reached at an observation point is a function of the distance of the point from the center of the dispersing mass, and the maximum values are reduced at greater distances.

SECTION VIII

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SECTION IX

NOMENCLATURE

Dimensions or units are shown to define the type of quantity. Actual usage will vary and these quantities may be converted to different units. In some cases, variables listed below may also appear in miscellaneous notation for limits of integration and dummy arithmetic function arguments.

a	=	spill location, offset on the surface from the center of the river (positive value in direction of positive y-axis)	cm
		collection of constant coefficients in concentration equation	$gm\text{-}sec/cm^3$
		parameter, limiting exponent for numerical representation	nd
		dissipation parameter	$cm^{2/3}/sec$
		half-width of interval containing dispersing mass	cm
a_i	=	coefficients in Hastings' approximation of error function (i=1,5)	nd
A	=	cross-sectional area of river channel; also given as $A(x,t)$ and $\bar{A}(x)$ for tidally averaged flow area	cm^2
		collection of constant coefficients in concentration equation	gms

b = half-width of river channel (w/2) cm

collection of constant coefficients in concentration equation $\mathrm{sec/cm^2}$

parameter, limiting exponent for numerical representation nd

interval over which instantaneous source is distributed in one-dimensional system cm

b_i = transformed or scaled coefficients in Hastings' approximation of error function (i=1,5) nd

c = concentration of pollutant at specified time and location; may also be steady state concentration or function of one to three spatial coordinates $\mathrm{gm/cm^3}$

$\bar{c}$ = average concentration for uniform distribution over particular volume of receiving water body $\mathrm{gm/cm^3}$

c_o = initial concentration $\mathrm{gm/cm^3}$

c_H = specified hazardous concentration $\mathrm{gm/cm^3}$

c_L = lower limit for concentrations of interest $\mathrm{gm/cm^3}$

d = depth of river channel cm

D = molecular diffusion coefficient cm^2/sec

D_{AB}^{o} = molecular diffusion coefficient cm^2/sec

e = constant, 2.718... nd

e_x = turbulent dispersion coefficient in longitudinal direction cm^2/sec

e_y = turbulent dispersion coefficient in lateral direction cm^2/sec

e_z = turbulent dispersion coefficient in vertical direction cm^2/sec

E = effective longitudinal dispersion coefficient, constant; or variable as $E(x,t)$ cm^2/sec

$\bar{E}(x)$ = time averaged longitudinal dispersion coefficient m^2/sec

E_D = estuary stratification parameter nd

E_t = dispersion coefficient primarily influenced by transverse velocity variations m^2/sec

E_v = dispersion coefficient predominantly affected by vertical velocity gradients m^2/sec

$erf(x)$ = error function, $\frac{2}{\sqrt{\pi}}\int_0^x e^{-\xi^2}\,d\xi$ nd

erfc(x)	=	error function complement, 1 - erf(x)	nd
f(t)	=	function of sinusoidal river velocity for tidal rivers	cm
$f(\xi)$	=	source strength per unit length in one dimensional system	gm/cm^3
F	=	Gaussian distribution function	nd
F_D	=	densimetric Froude number at entrance to estuary	nd
g	=	gravitational constant	cm/sec^2
G	=	function defined as collection of exponential terms in concentration equation for non-tidal rivers	nd
h	=	depth of river flow, also h_m	cm
I	=	value of integral expression in concentration equation; also, steady state value = I_{SS}	$sec^{-1/2}$
k	=	first-order decay coefficient	sec^{-1}
K	=	dispersion parameter	cm^2/sec
l	=	length scale characterizing the size of diffusing substance	cm
L	=	length scale of turbulent eddies	cm

		length of the salinity intrusion region of the estuary	cm
m	=	total mass in one-dimensional system, as amount released instantaneously, m, or as a distributed function m(x,t)	gm/sec^2
$\dot{m}$	=	constant release rate of discharging pollutant in one-dimensional system	gm/cm^2-sec
M	=	total mass of chemical released instantaneously at time t=0, also M(0)	gm
$M(x,y,z,t)$	=	mass distribution in space and time	gm
$M(t)$	=	total mass of substance remaining in environment after elapsed time t from release	gm
M	=	molecular weight	gm/g-mole
$\dot{M}$	=	constant pollutant discharge rate	gm/sec
M_B	=	molecular weight of solvent B	gm/g-mole
n	=	Manning roughness factor	$ft^{1/6}$
		integer value or fractional multiplier	nd
N	=	Brunt-Vaisalla frequency $=\sqrt{g\Omega}$	sec^{-1}
		constant of proportion	nd
$\bar{N}$	=	mean of Vaisalla frequency	sec^{-1}

p	=	coefficient in Hastings' approximation of error function	nd
P(b,η)	=	polynomial term in error function approximation	nd
P_T	=	volume of water entering estuary in flood tide (tidal prism)	cm^3
q	=	concentration as a function of time and position for a conservative substance	gm/cm^3
$\bar{q}^2$	=	$\bar{u}^2 + \bar{v}^2$, current fluctuations	cm^2/sec^2
Q	=	discharge, also Q(x,t)	cm^3/sec
Q_f	=	fresh water discharge, volume/time	cm^3/sec
Q(t)	=	total amount of substance discharged by a continuous release to the environment	gms
$\bar{Q}(x)$	=	time averaged discharge	cm^3/sec
r	=	scale factor or fractional value	nd
		pipe radius	cm
		transformation, $\frac{x^2}{4e_x} + \frac{y^2}{4e_y} + \frac{z^2}{4e_z}$	sec
r_{ij}^2	=	transformation, $\frac{x^2}{4e_x} + \beta_i^2 + \gamma_j^2$	sec
R_h	=	hydraulic radius	cm
s	=	scale factor	nd

transformation, $4(\pi)^{3/2}\sqrt{e_x e_y e_z}$ $cm^3/sec^{3/2}$

s = local salinity ppm

$\overset{\circ}{s}$ = dimensionless one-dimensional salinity gradient $\frac{s}{s_o}$ nd

s_o = salinity at mouth ppm

S = energy slope nd

t = time; elapsed time from start of spill sec

temperature °c

t_d = elapsed time required for the concentration at the spill location to reach a specified value; delay time sec

t_{mt} = total elapsed time from start to stop of a continuous discharge sec

t_p = tidal period sec

t_w = water temperature °c

$t_{1/2}$ = half-life sec

t_ρ = time required for Gaussian distribution to produce concentration at spill location equal to density of discharged substance sec

T = absolute temperature °k

T_b = normal boiling point °c

T_{br} = ratio, T_b/T_c nd

T_c = critical temperature °c, °k

T_r = reduced temperature (T/T_c) nd

T_t = diffusional time ratio for transverse spreading nd

T_v = diffusional time ratio for vertical spreading nd

T_w = water temperature °c

u = constant uniform cross-sectional river velocity, or variable or constant receiving water body bulk flow velocity component in x-direction cm/sec

U^* = shear velocity cm/sec

u_o = maximum tidal velocity knots

u_f = non-tidal component of water velocity cm/sec

u_m = mean oscillating flow velocity cm/sec

u_t = amplitude of superimposed sinusoidal tidal velocity cm/sec

v = receiving water body bulk flow velocity component in y-direction cm/sec

V = volume of receiving water body or portion of water body cm^3

V_o	=	initial volume	cm^3
V_A	=	molal volume of solute A at its normal boiling point	cm^3/g-mole
V_b	=	molar liquid volume at normal boiling point of solute	cm^3/g-mole
w	=	width of river channel	cm
		receiving water body bulk flow velocity component in z-direction	cm/sec
W	=	wind speed	cm/sec
$\bar{W}^2$	=	mean square of wind speed	cm^2/sec^2
x	=	longitudinal or downstream coordinate relative to river centerline at surface	cm
$\overset{\circ}{x}$	=	dimensionless ratio of distance from mouth to length of estuary	nd
x_c	=	limit distance for near field approximation; critical distance	cm
y	=	lateral or cross-stream coordinate relative to river centerline at surface	cm
z	=	depth coordinate (positive is down) relative to river centerline at surface	cm

Greek Symbols

α	=	longitudinal spatial coordinate relative to spill location	cm
		coefficient in longitudinal dispersion coefficient equation	nd
$\alpha(t)$	=	decay function given as ratio of total mass at time t to initial mass	nd
β	=	lateral spatial coordinate relative to spill location	cm
		transformation variable	(various)
		ratio of elapsed time from discharge to half-life of discharged substance	nd
		coefficient in longitudinal dispersion coefficient equation	nd
$\beta_1, \beta_2, \beta_3$	=	transformation variables	$sec^{1/2}$
β_j	=	coefficients in longitudinal dispersion coefficient equation	nd
β_{mt}	=	ratio of discharge interval (t_{mt}) to substance half-life	nd
γ	=	vertical spatial coordinate (positive is down) relative to spill location	cm
$\gamma_1, \gamma_2, \gamma_3$	=	transformation variables	$sec^{1/2}$

δ = phase lag (time to next high water slack) sec

small number nd

η = variable of error function approximation nd

η_B = viscosity of solvent B cp

η_{ij} = transformation variable in error function approximation nd

Θ = transformation variable nd

μ' = characteristic eddy velocity fluctuation cm/sec

μ_w = viscosity of water at temperature t_w cp

ξ = dummy variable for transformations and integration (various)

ξ_o = lower limit of integration (various)

ξ_s = upper limit of integration (various)

π = constant, 3.14159... nd

ρ = density of discharged substance gm/cm^3

ρ_1 = liquid molar density $g\text{-}mole/cm^3$

ρ_{1b} = molar density at boiling point $g\text{-}mole/cm^3$

ρ'_{1b} = density of solute at its normal boiling point gm/cm^3

ρ_v = vapor molar density $g\text{-}mole/cm^3$

σ = standard deviation of Gaussian distribution; also given as $\sigma_x, \sigma_y, \sigma_z$ for three-dimensional distributions — cm

$2\pi/t_p$ for use in tidal velocity expression — sec^{-1}

τ = elapsed time variable — sec

τ_o = wall shear stress — N/m^2

ϕ = dimensionless association factor of solvent B — nd

$\phi(x)$ = function to be represented by numerical approximation (i.e., error function where x is a dummy argument) — nd

$\phi^*(x)$ = numerical approximation of function $\phi(x)$ — nd

$\phi'(x)$ = error function integrand evaluated at x — nd

ω^2 = transformation, $\frac{u^2}{4e_x} + k$ — sec^{-1}

Ω = water body density gradient — cm^{-1}

Ω^2 = transformation, $u^2 + 4kE$ — cm^2/sec^2

APPENDIX A

OVERVIEW OF CHRIS COMPONENTS

1. INTRODUCTION

The Chemical Hazard Response Information System [2,8,9,10], known as CHRIS, and the Hazard Assessment Computer System[11] component of CHRIS, known as HACS, were developed by Arthur D. Little, Inc. for the U.S. Coast Guard to provide a systematic, simplified approach to identifying the appropriate processes governing a given chemical release and methods for estimating the hazard. One of the spill models originally formulated for use within CHRIS and HACS addressed the estimation of hazards caused by the accidental spill of a toxic chemical, miscible with water, on different types of receiving water bodies. Since this previous work formed the basis for the development of the spill model as described in this report, this appendix contains brief summaries of the components of CHRIS to provide additional background on the relationship of the individual water dispersion model to the approach for hazard estimation embodied in CHRIS.

CHRIS is designed overall to provide timely information essential for proper decision-making by responsible Coast Guard personnel and others during emergencies involving the water transport of hazardous chemicals. A secondary purpose is the provision of certain basic non-emergency-related information to support the Coast Guard in its efforts to achieve improved levels of safety in the bulk shipment of hazardous chemicals. CHRIS consists of four reference guides or manuals, a regional contingency plan, a hazard assessment computer system (HACS), and an organizational entity located at Coast Guard Headquarters. The four manuals contain chemical data, hazard assessment methods, and response guides. Regional data for the entire coastline are included in the Coastal Regional Contingency Plans. The headquarters staff operates the hazard assessment computer system and provides technical assistance on request by field personnel during emergencies. In addition, it is responsible for periodic update and maintenance of CHRIS.

2. A CONDENSED GUIDE TO CHEMICAL HAZARDS, CG-446-1[8]

This handbook, designated CG-446-1, Condensed Guide to Chemical Hazards, contains information to facilitate early response decisions during emergency situations. It is a compact, convenient source of chemical-related information with specific reference to bulk-shipped hazardous materials. The guide is intended primarily for use by port security personnel and others who may be the first to arrive at the site of an incident and need readily available, easily understood, descriptive information about the hazardous nature of the chemical and the situation confronted. It will assist those personnel in quickly determining proper, responsible actions that must be taken immediately to safeguard life and property and to reduce, insofar as possible, further contamination of the environment. The guide contains precautionary advice on the chemical and its characteristic physical and biological hazards so that field personnel can assess the threat as a prerequisite to determining subsequent large-scale action.

Since the Condensed Guide to Chemical Hazards is the only component of CHRIS that will be initially available at the scene of an accident, it includes a list of on-scene information needs that the Hazard Assessment Handbook

(CG-446-3) and HACS require as inputs. The on-scene information needs of the Hazard Assessment Handbook and HACS are listed in the Condensed Guide to Chemical Hazards (CG-446-1) as questions which must be answered and relayed to the user of the handbook or HACS as soon as possible.

3. HAZARDOUS CHEMICAL DATA, CG-446-2[2]

The Hazardous Chemical Data Manual, CG-446-2, is intended for use primarily by the On-Scene Coordinator's (OSC) office and the Regional and National Response Centers. It contains detailed, largely quantitative chemical, physical, and biological data necessary for formulating, evaluating, and carrying out response plans. The Hazardous Chemical Data Manual contains the hazard assessment code, which is essential to selecting the appropriate calculation procedures for the hazard assessment and lists the needed physical and chemical property data which are required to perform the hazard assessment calculations in CG-446-3.

4. HAZARD ASSESSMENT HANDBOOK, CG-446-3[9]

The Hazard Assessment Handbook contains manual methods for estimating the rate and quantity of hazardous chemicals that may be released under different situations. It also provides the means of predicting the threat that the chemicals present after release. It includes methods for predicting the resulting potential toxic, fire, and explosion effects by providing procedures for estimating the concentration of hazardous chemicals (both in water and in air) as a function of time and distance from the spill.

5. RESPONSE METHODS HANDBOOK, CG-446-4[10]

The Response Methods Handbook, CG-446-4, is a compendium of descriptive

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MATHEMATICAL DEVELOPMENT OF THE SPILL ASSESSMENT MODEL (SAM) FO--ETC(U)
FEB 80 R G POTTS, J H HAGOPIAN, C R WOODRUFF F08635-79-C-0084
UNCLASSIFIED AFESC/ESL-TR-80-07 NL

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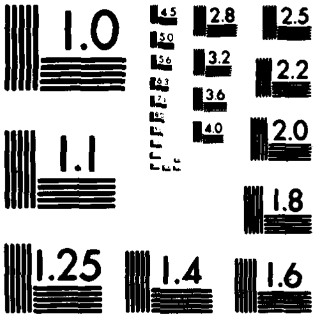

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information and technical data pertaining to methods of responding to threatened or actual spills of hazardous chemicals. The document has been written specifically for Coast Guard OSC personnel who have had some training or experience in pollution and hazard response. Emphasis has been placed on existing or prospectively available methodology. As new methods become available, the response handbook will be updated to include these new approaches.

In an actual emergency, an assessment of the likely extent of hazard, using the Hazard Assessment Handbook and/or HACS, will be used in the choice of the appropriate response methods suggested in the Response Methods Handbook.

6. DATA BASE FOR REGIONAL CONTINGENCY PLAN

The information in this data base is predominantly for use by OSC personnel. It contains data pertinent to a specific region, subregion, or locale. It will provide detailed information on resources that might be threatened and the availability of response equipment. Examples of such information include an inventory of physical resources and personnel; vulnerable or exposed resources (critical water-use areas); potential pollution sources, geographical and environmental features; cooperating organizations; and recognized experts with identified skills. A good deal of this regional-specific information is in the form of Regional Contingency Plans.

7. *HAZARD ASSESSMENT COMPUTER SYSTEM (HACS)*[11]

HACS is perhaps best described as the computerized counterpart of the CHRIS Hazardous Chemical Data Manual (CG-446-2) and Hazard Assessment Handbook (CG-446-3). It enables personnel at Coast Guard Headquarters to quickly obtain more detailed hazard evaluations than may be possible by means of

CG-446-3. Graphic output displays the relationships among spill concentration, thermal radiation, location, and time. This information may then be transmitted to field units and elsewhere by facsimile. Furthermore, HACS can be used for emergency discharge advance planning and the development and testing of improved hazard assessment methods.

Of concern is the evaluation of, and response to, any dangerous condition precipitated by accidents involving discharged chemicals which has, as a potential foreseeable consequence, harm or injury to life and/or property. A chemical discharged (or spilled) on water can create a hazard because of its flammability, its toxicity, or both. As the spilled material disperses and/or becomes diluted, the hazard normally decreases and disappears. It is important to know how far and fast the danger of fire or poisoning can spread and at what point the chemical ceases to be hazardous.

The processes of dispersion, evaporation, combustion, and the like, which are associated with the chemicals of concern, are quite complex and depend on many variables, not the least of which is the nature of the chemical itself. HACS offers a systematic and convenient approach to estimate the type and extent of hazard. The hazard estimate is given in terms of distance and times over which a toxic or flammable concentration of a given chemical may exist in water and in air, and the minimum safe distance between the spill site and people or combustible materials, should the chemical ignite and a fire ensue. HACS presently contains all necessary physical and chemical property data to permit hazard assessments to be performed for 900 commonly shipped chemicals.

a. Related Systems

The Hazard Assessment Computer System is comprised of a specific set of assessment models, chemical specific data and an overall system structure to provide data control and output displays. Two separate computer programs are used to define and produce independent displays of the chemical-specific data. Also to assist in obtaining the compound recognition code used to reference data for a particular chemical, a separate set of indices have been produced which enable a user of HACS to obtain a compound recognition code for a chemical given either the compound name or a synonym.

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