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Rapid Assessment of Potential Ground-Water Contamination Under *Emergency Response* Conditions

RAPID ASSESSMENT OF POTENTIAL GROUND-WATER CONTAMINATION
UNDER EMERGENCY RESPONSE CONDITIONS

by

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FOREWORD

The Exposure Assessment Group of EPA's Office of Research and Development has three main functions: 1) to conduct exposure assessments; 2) to review assessments and related documents; and 3) to develop guidelines for Agency exposure assessments. The activities under each of these functions are supported by and respond to the needs of the various EPA program offices. In relation to the third function, the Exposure Assessment Group sponsors projects for the purpose of developing or refining techniques used in exposure assessments. This study is one of these projects and was done for the Office of Emergency and Remedial Response.

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 established a national fund for the purpose of cleaning up spills and abandoned sites containing hazardous substances. When these sites are discovered, EPA must decide quickly if an urgent threat exists requiring immediate action. This project is intended to aid the Agency in making these decisions by providing a method for rapidly evaluating the human health and environmental threat caused by discharges to ground water. The Agency's final decision must also consider the threat caused by releases to the air and surface waters. The Exposure Assessment Group hopes to eventually provide similar methods which can be used to assess the threats associated with the other media as well.

James W. Falco, Director
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ABSTRACT

EMERGENCY RESPONSE actions at chemical spills and abandoned hazardous waste sites often require rapid assessment of the potential for ground-water contamination by the chemical or waste compound. This manual provides a rapid assessment methodology for performing such an evaluation within the 24-hour emergency response time frame so that emergency actions can be taken. The methodology consists of a decision flowchart, graphical (quantitative) procedures for estimating contaminant concentrations and travel times through soils and ground water, and guidelines for estimating required parameters representing critical contaminant and site characteristics.

The quantitative procedures for estimating contaminant transport are based on a variety of simplifying assumptions related to contaminant characteristics and the subsurface environment to conform to the data, time, and resource limitations expected during an emergency response. Consequently, the assessment methodology provides order-of-magnitude estimates of contaminant concentrations with time and distance below the land surface; the procedures are not intended to provide an indepth analysis of the complex fate and transport processes in the subsurface environment.

In addition to the components of the methodology, this manual discusses critical compound and site characteristics, describes assumptions and limitations of the procedures, provides auxiliary sources of information (to supplement this manual) and presents example applications. To effectively use this manual, potential users will need an understanding of the fundamental concepts of soil science, hydrogeology, and chemistry, in addition to an appreciation of the assumptions and limitations of the methodology. Familiarity and prior training in the use of this manual is highly recommended for efficient use during an emergency response situation.

v

FIGURES

TABLES

TABLES (Cont.)

ACKNOWLEDGMENTS

SECTION 1

INTRODUCTION

The purpose of this manual is to provide a methodology for estimating potential ground-water contamination, under emergency response conditions, at an abandoned hazardous waste or toxic chemical spill site. Specifically, this manual is designed for use by field personnel to quickly estimate how contaminant concentrations might change with time and distance from an emergency response site. The procedures include evaluation of critical contaminant and site charcteristics as input to an assessment methodology for analyzing the fate and movement of chemicals through both the unsaturated and saturated (i.e. ground water) soil zones. A graphical technique (i.e. nomograph) has been developed for contaminant movement through both the unsaturated and saturated (ground water) zones to provide a complete, integrated assessment methodology. Guidelines for evaluating critical waste and site characteristics are provided to allow estimation of needed nomograph parameters.

1.1 SCOPE AND LIMITATIONS OF THIS MANUAL

The phrase EMERGENCY RESPONSE is emphasized throughout this manual because it has been the over-riding criterion (and constraint) for selection, evaluation, and development of pollutant transport assessment methods and parameter evaluation techniques included herein. Emergency response situations require assessments of potential ground-water contamination to be completed in less than 24 hours. Consequently, extensive field sampling, laboratory analyses, data search and collection, and sophisticated computer analyses are generally impractical during this limited time frame. Although these extensive sampling and analysis activities may be initiated during the emergency response period, the results are not expected to be available for use in an emergency assessment.

The assessment procedures in this manual are designed to allow emergency response personnel to make a first-cut, order-of-magnitude estimate of the potential extent of contamination from a waste site or chemical spill within the 24-hour emergency response time frame. These procedures are not intended to provide a definitive, indepth analysis of the complex fate and transport processes of contaminants in the subsurface environment.

The primary goal of this manual is to provide the basis for determining the need for emergency actions, such as emergency sampling, containment/removal, drinking water restrictions, etc. in order to preclude or minimize human exposure from ground-water contamination at an emergency response site. Two

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specific emergency response situations are envisioned where the assessment
procedures in this manual would be applied.

1. Discovery of an abandoned hazardous waste site where an assessment
   of the potential extent of the waste plume is needed within the
   emergency response time frame.

2. Spill (or leakage) of a toxic waste or chemical where the potential
   for ground-water contamination and/or the extent of contamination
   must be assessed within the emergency response time frame.

Time and resource limitations expected during an emergency response have
required a number of simplifying assumptions in our assessment procedures;
additional simplifications may be needed by the user due to limited data and
information available at a particular emergency response site. The major
assumptions incorporated into the assessment procedures in this manual are
as follows:

1. Homogeneous and isotropic properties are assumed for both the
   unsaturated and saturated zones (or media).

2. Steady and uniform flow is assumed in both the unsaturated and
   saturated zones.

3. Flow and contaminant movement are considered only in the vertical
   direction in the unsaturated zone and the horizontal direction in
   the saturated zone.

4. All contaminants are assumed to be water-soluble and exist in
   concentrations that do not significantly affect water movement.

A variety of other assumptions and limitations in the procedures are further
discussed in Section 3.5. The user should carefully review all the
assumptions and limitations, and must make specific judgements as to their
validity for the specific site, contaminant(s), and emergency situation
being analyzed. Perhaps the most critical aspect of an emergency response
situation will be the ability of the user to adequately characterize, within
the 24-hour time frame, the subsurface media (e.g. heterogeneities, depth to
ground water, soil/aquifer properties, aquifer thickness) through which the
contaminants may move. Consequently, access and/or availability of data,
expertise, and familiarity with local, site-specific soils and hydrogeologic
conditions is critical to the successful application of the assessment
procedures in this manual.

1.2 REQUIRED USER BACKGROUND, TRAINING, and PREPARATION

Effective use of this manual requires an understanding of a mix of
disciplines, such as hydrology, hydrogeology, soil science, chemistry, on
the part of the intended user, and sufficient familiarity or training with
the techniques, procedures, and auxiliary sources of information described
herein. Moreover, this manual is not intended to be a primer on pollutant

fate and movement through soils and ground water; a variety of excellent introductory textbooks and reports in these areas are available to the potential user to provide the needed background (e.g., Freeze and Cherry, 1979; EPA, 1981; Thibodeaux, 1979).

Ideally, academic training in any one of the above disciplines supplemented with experience, job training, and/or exposure (e.g. short course attendance) in the other disciplines provides a profile of the recommended background for a user. Alternatively, an engineering or science undergraduate degree with appropriate training is acceptable as long as a basic understanding in the following areas is included:

a. the hydrologic cycle and its components

b. hydrogeologic concepts, processes, and terminology related to ground-water movement

c. soil science concepts related to soil processes and water movement

d. chemical processes, parameters, and terminology

e. mathematical capabilities and skills in the use of scientific hand calculators.

In many emergency response situations, the user will have access to experts in the above disciplines to provide guidance in parameter evaluation. Thus, the user must have sufficient comprehension of the appropriate terminology in order to communicate effectively with the experts and "ask the right questions!"

User training and preparation is needed to develop familiarity with the assessment procedures described in this manual and the wide range of auxiliary sources of information that supplement and complement the parameter evaluation guidelines in Section 4. In essence, the user should be able to ask and answer the question - "What information do I need and where can I get it?"

Training and/or familiarity with the specific procedures described herein is absolutely essential to effectively use this manual. Without prior study users cannot expect to use this manual for assessing potential ground-water contamination within a 24-hour period. Although every effort has been made to simplify the procedures and parameter evaluation guidelines, prior study is needed to become familiar with the assumptions/limitations, the step-by-step calculations, the application of the nomographs, the parameter evaluation guidelines, and the auxiliary sources of information. Also, knowledge of the most sensitive, critical parameters will allow the user to allocate data search efforts most effectively.

Familiarity with supplementary sources of information cannot be over-emphasized. Section 2.4 describes a variety of handbooks and data bases from which contaminant characteristics (and input parameters) can be evaluated or estimated. Precious time can be saved if the user is knowledge-

able about which sources are most likely to contain the information he is seeking.

Since site characterization may require the greatest effort during an emergency assessment, preparation of a regional or local data base on meteorology, hydrologic characteristics, soils/aquifer properties, ground-water characteristics, prior hydrology/hydrogeologic studies, and local experts (i.e. contacts and phone numbers) could considerably shorten the time needed to obtain data and improve the resulting parameter estimates. A similar, regional data base for the characteristics of wastes and chemicals produced in, or transported through, the region would be extremely valuable. Recommendations for the contents and format of such a regional data base have been developed for EPA (Battelle PNL, 1982a).

1.3 FORMAT OF THE MANUAL

Section 2 describes the types of hazardous waste and spill situations for which the assessment procedures are designed, and provides a methodology flow chart to guide an application. An overview of critical compound and site characteristics is provided along with a discussion of recommended sources of information. Section 3 describes both the unsaturated and saturated zone methodologies and the assessment nomograph. A detailed description of the assessment methodology. Section 3 also discusses linkage of unsaturated and saturated zone assessments and the assumptions and limitations of the assessment procedures - these should be carefully reviewed and understood by the user.

Section 4 provides guidelines for estimating the input parameters for both the unsaturated and saturated zone assessments. Emphasis is placed on obtaining local site and compound specific data in order to obtain realistic parameter estimates. However, quantitative guidelines are provided for most parameters as a last resort if no other information is available.

Section 5 presents example applications for the assessment nomograph for both zones and demonstrates linkage procedures. Section 6 includes cited references, Appendix A provides a description of the SCS Curve Number procedure for estimating surface runoff; Appendix B is a glossary of terms; and Appendix C provides blank worksheets and copies of enlarged nomographs for ease of use during an application.

1.4 CAVEAT

Although all efforts have been made to insure the accuracy and reliability of the methods and data included in this manual, the ultimate responsibility for accuracy of the final predictions must rest with the user. Since parameter estimates can range within wide limits, especially under the resource and time constraints of an emergency response, the user should assess the effect of methodology assumptions and parameter variability on predicted concentrations for the specific site. The methodology predictions must be evaluated with common sense, engineering judgement and fundamental principles of soil science, hydrogeology, and chemistry. Accordingly, neither the authors nor Anderson-Nichols assume liability from use of the methods and/or data described in this manual.

SECTION 2

OVERVIEW OF RAPID ASSESSMENT METHODOLOGY

An emergency response to releases of hazardous substances is generally comprised of three steps - characterization, assessment, mitigation - defined as follows (Battelle PNL, 1982a):

o   Characterization - the acquisition, compilation, and processing of data to describe the scene so that a valid assessment of alternative actions can be made.

o   Assessment - an analysis of the severity of an incident; the evaluation of possible response actions for effectiveness and environmental impact.

o   Mitigation - the implementation of the best response action and followup activities.

The assessment procedures for potential ground-water contamination in this manual draw upon data and information developed in the characterization phase in order to provide a tool for performing parts of the assessment phase when ground-water contamination is suspect. The EPA Field Guide for Scientific Support Activities Associated with Superfund Emergency Response (Battelle PNL, 1982a) provides an excellent framework within which to view these procedures as part of the arsenal of the emergency response team for assessments of hazardous substance releases. This field guide identifies the calculation of transport rates of hazardous materials as an important element in the assessment phase. When subsurface fate and movement of hazardous substances is important at an emergency response site, these calculations can be made with the procedures described herein based on the methodology assumptions and data expected to be available within the emergency response time frame.

2.1   APPLICATION SCENARIOS

Ground-water contamination by hazardous materials may result from surface spills; seepage from waste injection operations, waste storage/burial sites; and leaks from underground containers (i.e., waste or storage) or pipelines. The rapid assessment procedures are designed for application in two typical scenarios, or cases, based on the temporal nature of the release:

Case 1 Analysis - Typically a hazardous waste site or chemical/waste storage facility where the release is relatively continuous and constant over an extended period of time (e.g. years).

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Case 2 Analysis - Typically a spill incident (or a short-term release
from a storage facility) where the release can be assumed constant
over a relatively short span of time (e.g. weeks, months) producing
a pulse-type release.

The assumption of a constant release either on a continuous or pulse basis
is necessary for the analytical solutions from which the nomographs have
been developed. Consequently, although actual releases will be
time-varying, the user will need to approximate the actual release by either
the Case 1 or Case 2 assumptions above in order to perform an assessment
within the emergency response time frame. (See Section 3 for further
discussion.)

Superimposed on the temporal nature of the release is the time period of
concern for the assessments and the associated quantities of the forces
driving the movement of the contaminant. In most cases, the driving force
will be water movement through the soil to ground water; for large volume
spills the mass of the material may be sufficient to move through the soil.

The time period can vary from an assessment of the historical movement and
current extent of the contaminant plume, to a projection of the plume at
some time in the future. For the discovery of an abandoned hazardous waste
site, the user may need to evaluate the current extent of contamination
based on the age of the site, the period of release, and ground-water
recharge estimates during the past; whereas, for a spill situation the user
may need to project the future movement of the plume based on precipitation
forecasts and resulting expected recharge. Thus, the time period of concern
and the temporal nature of the release jointly determine the appropriate
type of analysis (i.e., Case 1 vs. Case 2) and parameter estimates for the
driving force behind contaminant movement.

2.2 METHODOLOGY FLOWCHART

The overall flowchart for the rapid assessment methodology is shown in
Figure 2.1. Prior to initiating application of these procedures, the
On-Scene Coordinator (OSC) at the emergency response site must determine
that (1) the potential for ground-water contamination exists, or (2)
contaminants have reached ground water, and (3) an assessment of the
potential or current extent of contamination must be made within the 24-hour
emergency response time frame. These decisions will be based on the results
of the characterization phase of the emergency response effort and will
depend on current conditions (e.g., current contamination of wells or
streams, weather forecasts), compound characteristics (e.g., toxicity,
solubility, sorption, volatility), and site characteristics (e.g., depth to
ground-water, soil/aquifer characteristics, distance to drinking water wells
and streams). If no emergency assessment is deemed necessary, the
procedures in this manual should not be used, except as preliminary guidance
for subsequent detailed sampling, analysis, and investigations possibly
including numerical modeling techniques.

If an emergency assessment is deemed necessary, the steps in Figure 2.1
should be followed as discussed below:

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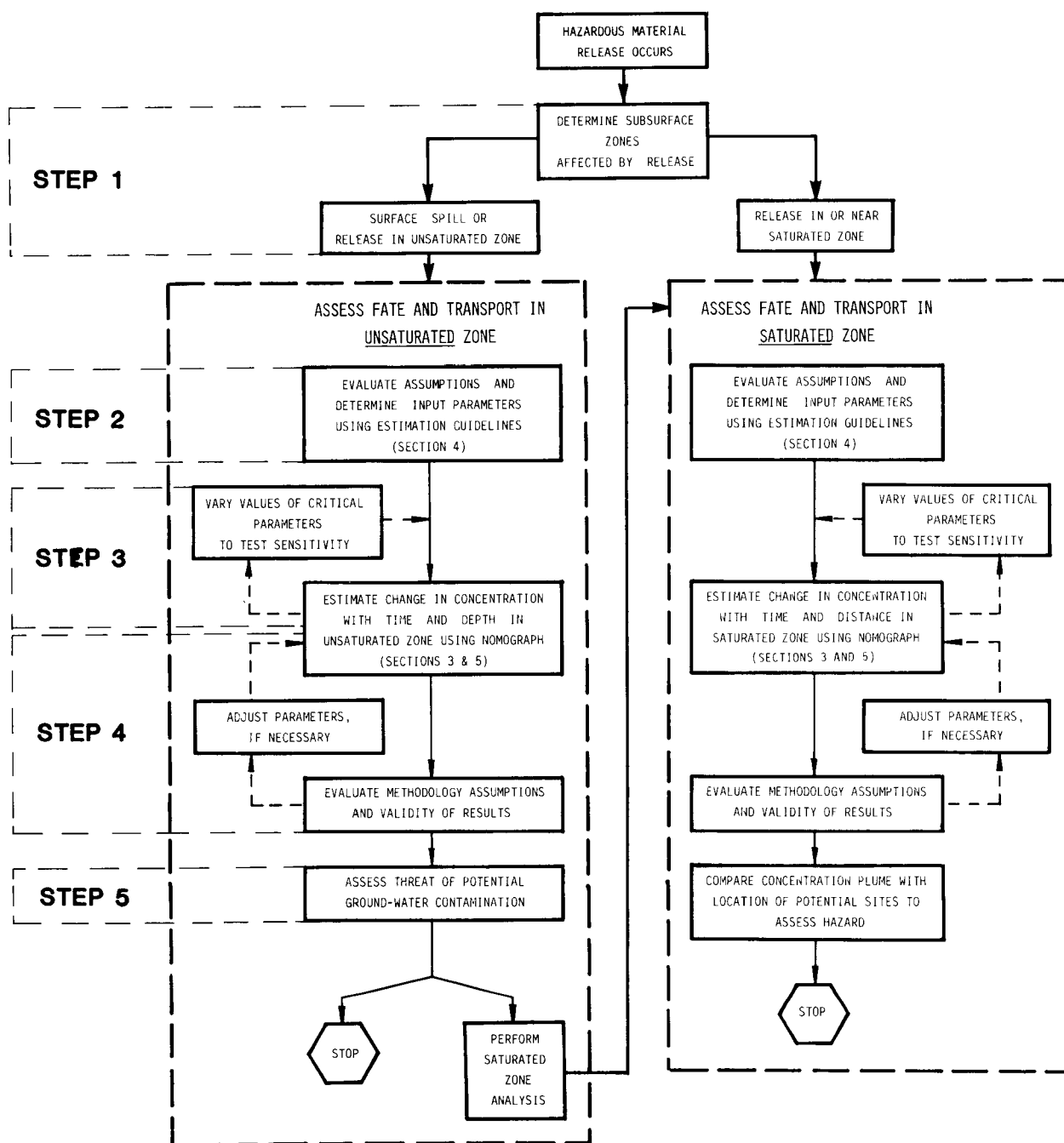
Figure 2.1   Flow Chart for Rapid Assessment of Potential Ground-Water
Contaminant Under Emergency Response Conditions.

STEP 1   involves the determination of which zone, unsaturated or
         saturated, will be affected by the contaminant release and
         which associated branch to follow in the flowchart. Most
         surface and near-surface releases will need to move through the
         unsaturated zone before reaching ground water; thus an
         unsaturated zone analysis (left branch in Figure 2.1) will be
         needed. For shallow ground-water depths, highly permeable
         soils, and/or highly fractured surface materials, the user may
         choose to ignore the unsaturated zone and assume direct release
         to the saturated, ground-water zone. This assumption ignores
         any attenuation or retardation in the unsaturated zone and, in
         many cases, will over-estimate actual concentrations reaching
         ground water.

STEP 2   involves an initial evaluation of the methodology assumptions
         (both unsaturated and saturated zones) for the specific site,
         and estimation of the nomograph input parameters based on the
         guidelines in Section 4. These two aspects are closely linked
         since parameter values can be adjusted to partially compensate
         for certain assumptions and limitations. However, significant
         parameter uncertainties should be identified early in the
         application so that associated impacts can be assessed.

STEP 3   includes calculation of concentrations with time and distance
         using the nomograph described in Section 3. For the
         unsaturated zone the depth to ground water will usually be the
         distance measurement of interest; for the saturated zone
         horizontal distances to nearby wells or streams may be needed.
         Sensitivity analyses should be performed on critical parameters
         (e.g., decay rate and retardation in the unsaturated zone,
         ground-water velocity in the saturated zone) in order to assess
         the effects of possible inaccuracies in parameter estimation.

STEP 4   requires the user to re-evaluate the methodology assumptions
         based on the predicted concentrations and results of
         sensitivity analyses. Further parameter adjustments and
         re-calculation of concentrations may be necessary. This is a
         critical step since the predictions will be used next to assess
         the potential or current extent of ground-water contamination.

STEP 5   provides the assessment results upon which to make decisions on
         needed emergency response actions. The need for an emergency
         response, and the possible alternative actions, are decisions
         to be made by the On-Scene Coordinator and other emergency
         personnel which are not addressed in this manual. For
         unsaturated zone analysis, concentration estimates for various
         depths will indicate if the contaminant will reach ground water
         at levels and within the time frame where emergency response
         actions may be needed. If ground-water contamination is
         predicted the user may need to perform a saturated zone
         analysis, using the results of the unsaturated zone analysis as
         input to estimate the contaminant plume migration in ground

water. The results of the saturated zone analysis can provide the concentrations and associated travel times at potential impact sites (e.g., wells, streams) where human exposure or ecological impacts may occur.

Complete application of the assessment procedures may require a number of iterations of the steps discussed above, as new data becomes available or as additional questions arise from the emergency situation. Following the step-by-step procedures outlined above and shown in Figure 2.1 will allow the user to perform consistent assessments of potential ground-water contamination in a variety of circumstances.

2.3 CRITICAL COMPOUND AND SITE CHARACTERISTICS

The extent of contaminant fate and transport following releases to the land surface and subsurface depends upon a variety of critical compound and site characteristics. Table 2.1 lists the major characteristics of concern for determining potential ground-water contamination at a specific site. This section briefly describes the compound and site characteristics listed in Table 2.1 to provide the user with an understanding of the types of information needed to perform a valid assessment. Guidelines for translating these characteristics into specific parameter values required by the assessment procedures are provided in Section 4.

2.3.1 Critical Compound Characteristics

To assess the potential for ground-water contamination in an emergency response situation, several properties of the compound or waste must first be determined. Much of this information may be difficult to accurately quantify within a 24-hour time frame, but it is likely that an applicable range of values can be estimated. Some properties are used directly in the assessment or to estimate parameters, while others are needed to interpret the results. Those characteristics deemed crucial to an informed assessment and listed in Table 2.1 are discussed below:

1. Contaminant Identity

   The identities of the contaminants must be known to determine those physical/chemical properties necessary for assessing pollutant fate and migration. The physical state of the contaminant (gas, liquid, or solid) should be assessed as part of the identification process. Within the emergency response time frame, it may be possible to identify only general classes of chemicals rather than specific compounds. In such instances, parameter estimation will be especially difficult.

2. Extent of the Contamination

   The extent of the contamination must be defined to determine the source term used in estimating transport into the soil and ground water. This assessment should provide an estimate of the mass of the pollutant entering, or potentially entering, the subsurface environment by adjusting for volatilization into the air, runoff, and containment or removal measures on the land surface,

TABLE 2.1 CRITICAL COMPOUND AND SITE CHARACTERISTICS

Critical Compound Characteristics

    1.   Contaminant Identity and Physical State

    2.   Extent of the Contamination

    3.   Solubility

    4.   Adsorption

    5.   Degradation

    6.   Toxicity

    7.   Concentration and Loading

    8.   Density, Viscosity, and Temperature

Critical Site Characteristics (Applicable to Both the Unsaturated and
    Saturated Zones Unless Otherwise Indicated)

    1.   Identity of Subsurface Medium

    2.   Age of Site

    3.   Distances to Wells, Streams, Property Boundaries

    4.   Porosity

    5.   Infiltration, Net Recharge, and Volumetric Water Content
        (Unsaturated Zone Only)

    6.   Bulk Density

    7.   Hydraulic Conductivity (Saturated Zone Only)

    8.   Chemical Characteristics of Medium

    9.   Dispersion

  10.   Depth to Ground Water (Unsaturated Zone Only)

  11.   Hydraulic Gradient (Saturated Zone Only)

  12.   Effective Aquifer Thickness (Saturated Zone Only)

  13.   Structural and Geologic Features

if necessary. Information on the volatility and reactivity of the waste may be required in making this assessment. In addition, the cross-sectional area of the spill or the disposal site should be ascertained.

3.   Solubility

The solubility of a compound affects its mobility in the soil and ground water. The release of the contaminant from a landfill or surface spill is usually controlled by its tendency to dissolve in the water moving through the soil. A material's solubility may also affect the ease with which it can adsorb on soil particles, with less soluble wastes being more easily adsorbed. Solubility generally provides an upper limit on dissolved concentrations that can be found in the soil environment. The existence of solvents other than water should also be determined since it can affect the compound's miscibility with soil water and ground water.

4.   Adsorption

Adsorption can be a significant means of retarding contaminant movement through the soil or ground water. It is a property dependent upon both the nature of the compound and the soil. Adsorption capabilities for organic, nonionic compounds are often described in terms of adsorption (or partition) coefficients for a particular compound/soil combination. These coefficients are often estimated from the organic carbon (or organic matter) content of the soil and the organic carbon partition coefficient (which in turn can be estimated from compound characteristics such as the octanol/water partition coefficient). Adsorption of ionic compounds is also a function of ion exchange capacities and clay type and content. This is especially important for soils or media with low organic matter.

5.   Degradation

Degradation by both chemical and biological mechanisms is important because it can prevent contaminants from reaching ground water and can reduce levels of contaminants already present. Common degradation mechanisms in the environment are hydrolysis, photolysis, biodegradation, chemical oxidation, and radioactive decay. Hydrolysis and chemical oxidation are important primarily for contaminants in soils and saturated media. Photolysis can occur only in surface waters or on the surface of the soil. Biodegradation is most important in surface waters and in the top few feet of soil where bacterial concentrations are high; however, anaerobic decomposition in deep soils and ground water is possible. Radioactive decay occurs in all environments under all conditions.

6. Toxicity

To assess the hazard of any predicted or observed ground-water contamination, the toxicity of the pollutants must be determined. Since nearly all chemicals are toxic at very high concentrations, the concern in this assessment is for materials that are moderately to severely toxic or are carcinogenic, mutagenic, or teratogenic to humans or aquatic organisms.

7. Concentration and Release/Loading Rate

Compound concentrations and volume or release/loading rates from a spill or waste site are especially important because of the effects on other characteristics and the extent of contamination. Concentration will affect solubility, adsorption, degradation, and toxicity. Since many of these characteristics are usually measured at low concentrations and/or in aqueous solutions, changes at high concentrations can be significant, such as exceeding solubility limits or adsorption capacities, or reducing effective microbial populations. Low volume releases from spills may only contaminate a few feet of soil which could be removed by excavation; whereas large volume and/or continuous releases can result in much larger scale contamination.

8. Density, Viscosity, and Temperature

These compound parameters are important in evaluating the mixing characteristics of the contaminant in soil water and ground water. Differences in these properties between the water and the contaminant can lead to density stratification, floating, or sinking of materials which will significantly impact transport behavior. Major differences in these characteristics may require an evaluation of the validity of the assessments which assume contaminant transport with the water movement.

2.3.2 Critical Site Characteristics

To assess potential ground-water contamination at a hazardous waste or spill site, a number of site characteristics listed in Table 2.1 are important in addition to the waste characteristics discussed above. Critical site properties for both the unsaturated and saturated zones are identified and briefly discussed below. Many of the parameters which define important site characteristics are shared by both subsurface zones, although the values for the parameters may be different for each zone. The discussions are intended to provide an overview of the information needed to characterize an emergency response site in appropriate detail to estimate contaminant transport and fate in the subsurface environment; specific guidelines on parameter estimation are presented in Section 4.

1. Identity of Subsurface Medium (Unsaturated and Saturated Zones)

Perhaps the most critical site characteristics which must be determined is the dominant material types of the subsurface zones.

While the subsurface materials for either zone will rarely be homogeneous, it is necessary to identify the major soil or rock types in order to assign reasonable values to such parameters as porosity, bulk density, hydraulic conductivity, dispersion coefficients, and chemical characteristics.

2. Age of the Site (Unsaturated and Saturated Zones)

The age of the site will be most important in analyzing newly-discovered landfills, uncontrolled waste disposal sites, or leaking chemical storage facilities. The extent of pollutant migration at the emergency response site cannot be adequately assessed without knowledge of the length of time that contamination has been occurring, unless other data are available. Many surface chemical spills are investigated immediately after their occurrence and thus the age of the incident is known.

3. Distances (Unsaturated and Saturated Zones)

Distances to water wells, streams, and property boundaries from the hazardous waste or spill site are fundamental concerns in an emergency response. This information represents horizontal distances that the waste material must travel on the land surface or in the ground, before reaching potential receptor sites of concern.

4. Porosity

The total porosity, usually stated as a fraction or percent, is that portion of the total volume of the material that is made up of voids (air) and water. In determining the retardation coefficient, a measure of adsorptive capabilities, the total porosity of the aquifer is needed. Due to dead-end or unconnected pores, effective porosity is somewhat less than total porosity. Effective porosity is often estimated as the specific yield in unconfined aquifers which is the quantity of water that will drain from a unit volume of aquifer under the influence of gravity. Effective porosity is required for the calculation of the interstitial pore-water velocity in ground water based on Darcy's Equation.

5. Infiltration, Net Recharge, and Volumetric Water Content (Unsaturated Zone Only)

Infiltration and net recharge refer to water movement below the land surface to the unsaturated soil zone and ground water. Infiltration is generally greater than net recharge since it includes evaporation and transpiration quantities which are usually deducted to estimate net recharge to ground water. Both of these components are a function of climatic, topographic and soil properties, and are important in estimating contaminant movement into and through the unsaturated zone to ground water. Their

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relative importance depends on the time frame of the analysis (See Section 4).

The volumetric water content is the volume of water in a given volume of media, usually expressed as a fraction or percent. It depends on properties of the media and the water flux estimated by infiltration or net recharge. The volumetric water content is used in calculating the water movement through the unsaturated zone (pore water velocity) and the retardation coefficient. In saturated media, the volumetric water content equals total porosity.

6. Bulk Density (Unsaturated and Saturated Zones)

The bulk density of the medium is required in calculating the retardation factor, a measure of adsorption processes. The bulk density is the dry mass per unit volume of the medium (soil or aquifer), i.e., neglecting the mass of the water.

7. Hydraulic Conductivity (Saturated Zone)

The velocity of ground-water flow is essential to assessing the spread of contamination; it is an especially sensitive parameter for plume migration in the saturated zone. The hydraulic conductivity (or permeability) of the aquifer is needed to estimate flow velocity based on Darcy's Equation. It is a measure of the volume of liquid that can flow through a unit area of media with time; values can range over nine orders of magnitude depending on the nature of the media. Heterogeneous conditions produce large spatial variations in hydraulic conductivity, making estimation of a single, effective value extremely difficult.

In the unsaturated zone, conductivity is an extreme function of soil moisture, increasing by orders of magnitude as moisture content increases. This indicates the difficulty in assessing dynamic pollutant transport through the unsaturated zone as a function of dynamic soil moisture conditions.

8. Chemical Characteristics of Medium (Unsaturated and Saturated Zones)

The primary chemical characteristics of the medium include organic carbon content, ion exchange capacity, clay type and clay content. These properties are used in conjunction with the adsorption characteristics of the compound (as discussed in Section 2.3.1) to allow formulation of an appropriate partition coefficient for the specific compound/medium combination. The partition coefficient is used with bulk density, and either total porosity (saturated zone) or volumetric water content (unsaturated zone) to calculate a retardation factor, to represent the impact of adsorption on retarding contaminant movement through the medium.

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9. Dispersion (Unsaturated and Saturated Zones)

Hydrodynamic dispersion in subsurface media is a phenomenon that causes the spreading of a contaminant. The complicated system of interconnected passages comprising a porous media system causes a continuous division of the contaminant mass into finer offshoots. Variations in the local velocity (both magnitude and direction) along and between these tortuous flow paths gives rise to this ever increasing spreading on the microscopic scale. On a larger or macroscopic scale, inhomogeneity due to variations in permeability and porosity also gives rise to further spreading. On a megascopic scale, the effects of layering and the associated differences in permeabilities and porosities can give rise to further spreading (Pickens, et al, 1977).

Dispersion is often considered together with molecular diffusion in determining a dispersion coefficient. Because the actual spread of a contaminant depends on inhomogeneity at various scales in addition to the tortuosity and local velocity variation on a microscopic scale, the selection and measurement of the dispersion parameter (i.e., dispersivity) should be related to the scale and detail of the modeling effort. This dependence on scale is demonstrated by the fact that dispersivity values measured in the laboratory can range from 10^{-2} to 1 cm, while field values can range from 10's to 100's of meters.

10. Depth to Ground Water (Unsaturated Zone)

The depth to ground water must be estimated in order to evaluate the likelihood that contaminants moving through the unsaturated soil will reach the ground water. Seasonal fluctuations, if significant, should be identified, as well as the impacts of pumping and recharge sources, natural or man-made.

11. Hydraulic Gradient (Saturated Zone)

To determine the magnitude and direction of ground-water flow, the hydraulic gradient must be known. It is the slope of the water table in an unconfined aquifer, or the piezometric surface for a confined aquifer. As for the ground-water depth, the effects of pumping and recharge should be considered in estimating the hydraulic gradient since these actions can reverse expected ground-water flow directions.

12. Effective Aquifer Thickness (Saturated Zone)

The available zone of mixing in the aquifer is described using an effective aquifer thickness. For good mixing between the ground water and the contaminant, this effective thickness may equal the actual total thickness of the aquifer, but in many cases it will be considerably less. In cases where the pollutant is of a significantly different density than water, the extent of mixing

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may be reduced and the contaminant plume will be concentrated over only a portion of the aquifer's thickness.

13. **Structural & Geologic Features (Unsaturated & Saturated Zones)**

A general assessment of the soils, topographic and geologic environment of the study site is necessary to effectively evaluate the potential for ground-water contamination. Rapid assessments made within an emergency response time frame must assume homogeneous conditions due to time constraints, but heterogeneous properties will retard or increase contaminant migration and should be at least qualitatively assessed. Folds, faults, fractures, sinkholes, clay lenses, and soil variations are examples of features that should be considered when estimating appropriate ranges of parameters used in the rapid assessment methodology.

2.4 AUXILIARY SOURCES OF INFORMATION

To obtain the data necessary to evaluate critical compound and site characteristics during an emergency response, a variety of information sources should be consulted prior to and during the emergency. As noted in Section 1.2, the need to be familiar with the various sources of information that might be needed during an emergency response cannot be over-emphasized. The EPA Field Guide (Battelle PNL, 1982a) mentioned previously includes a useful check-list of activities for chemical characterization that should be performed before and between emergency responses, during the response, and following the response; an analogous checklist is provided for hydrologic assessments. In support of our recommendations, the EPA Field Guide also emphasizes the importance of pre-emergency planning and preparation especially in the collection and aggregation of data sources for compound and site characterization. This guide should be an important part of the library of an emergency response team.

This manual is not intended to be a stand-alone document since the supporting data that might be needed in an emergency response would fill multiple volumes many times the size of this report. The sections below describe various information sources for both compound and site characteristics; these sources will be further referenced in the specific parameter estimation guidelines in Section 4.

2.4.1 Sources of Compound Characterization Information

During an emergency response, data on waste characteristics are available from five major sources:

1. Records

2. Onsite Observations

3. Analyses

4. Handbooks and Data Bases

5. Experts

These information sources must be applied jointly to determine the necessary input data for a ground-water contamination assessment. For example, transportation records may first be used to determine the chemical identity of a spilled cargo of waste before consulting a data base for a list of the physical/chemical properties of the waste. Much of the information in this section is published in the chemical characterization section of the EPA Field Guide, to which the user is referred for additional sources.

1. Records

Records can provide the most rapid, positive identification of the materials involved at an emergency, and, if available, should be the preferred means of identification. A variety of useful records (e.g., shipping papers and transportation labels) are now required when transporting hazardous materials. Transportation records contain information on the quantities of hazardous materials transported and may be used to estimate quantities involved in emergencies. A complete description of available records and how to use them in identifying spilled material is provided by Huibregtse, et al, (1977). Also, the Association of American Railroads is developing a computerized tracking system for rapidly identifying railcars containing hazardous materials (Guinan 1980). The use of records to identify chemicals present at uncontrolled waste sites is much more difficult. Waste manifests, which describe each shipment of waste received at a facility, are a possible source. In many cases, however, these have only recently been required.

2. Onsite Observations

Observable characteristics such as odor, color, density, and reaction may be useful in rapidly identifying an unknown material. An excellent method of quick identification of spilled materials based on easily observable characteristics is presented in the Field Detection and Damage Assessment Manual for Oil and Hazardous Materials Spills (EPA 1972). Over 300 hazardous materials are identified by odor, color, reaction, etc.

The U.S. Coast Guard Chemical Hazard Response Information System (CHRIS) Manual CG-446-1 and CG-446-2 (U.S.C.G. 1974a, 1974b) describes observable characteristics of approximately 900 hazardous chemicals. The OHM-TADS data system maintained by EPA can be used to identify chemical substances based on observable characteristics. Physical properties of the unknown material (physical state, odor, color turbidity, miscibility, reactions) are input to the

computer system, which then performs a search to obtain possible identities.

It should be noted that the use of observable characteristics may be limited to identifying general classes of chemicals rather than specific compounds.

Onsite observations may also be important in establishing the extent of the contamination. Aerial photography and remote sensing may be needed to supplement ground observations in detecting the boundaries of a large spill or dump site, but such information may not be available within the 24-hour emergency response time frame.

3. Analyses

Analytical methods may be employed if other methods fail to identify the contaminants present. In emergency conditions where rapid response is required, the available techniques may be limited to qualitative field methods. Laboratory methods, while providing more definitive results, require considerably more time. Mobile laboratories have now made many complex instrumental methods available for use in the field, helping to reduce the time requirements of laboratory analysis.

The Field Detection and Damage Assessment Manual for Hazardous Materials Spills (EPA 1972) describes analytic tests that may be used in the field to identify chemicals. A variety of commercial products are currently available for infield detection and identification of hazardous materials. These products include portable spectrophotometers, ion-specific electrodes, gas chromatographs, and organic vapor analyzers. Information on such systems can be obtained from manufacturers and scientific supply houses.

Once the identity of the contaminant is known, analytical methods can be used in conjunction with a sampling program to determine the extent of the contamination. Under emergency response conditions, maximum use must be made of existing sampling sites such as wells, ponds, drainage ditches, runoff collection devices, and so on. Hand or gasoline powered augers provide a rapid means of quickly obtaining subsurface samples over a large area. Sampling techniques are described in EPA (1980).

4. Handbooks and Data Bases

Handbooks and data bases are an excellent source of physical/chemical data on hazardous wastes including toxicities, solubilities, densities, degradation rates, reactivities, volatilities, and adsorption data. As were previously discussed, data bases and handbooks also aid in identifying wastes based on observable characteristics. The data source descriptions provided below were taken largely from the EPA Field Guide:

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Handbooks -

CHRIS, the Coast Guard Hazardous Chemical Data Manuals CG 446-1 and CG 446-2, are excellent sources of data on approximately 900 hazardous materials. The data contained in these and other CHRIS manuals are designed for use with the Coast Guard's Hazard Assessment Computer System (HACS), a computerized simulation system that models the physical behavior of chemical spills and provides information describing the extent of the hazard associated with these spills (Parnarouskis et al 1980).

Manual CG-446-1, A Condensed Guide to Chemical Hazards, contains a summary listing of physical/chemical properties of several hazardous materials. It is designed to be carried to the scene of an accident. Manual CG-446-2, Hazardous Chemical Data, contains detailed information on the properties of hazardous chemicals.

The EPA Field Detection and Damage Assessment Manual for Oil and Hazardous Materials Spills (EPA 1972) is useful for supplying data needed for identifying any of 329 hazardous materials in the field.

The Handbook of Environmental Data on Organic Chemicals (Verschueren 1977) is an excellent source of data describing the behavior of over 1,000 organic chemicals in the environment. This is perhaps the most complete collection of environmental chemical data that can be easily taken into the field.

Dangerous Properties of Industrial Materials (Sax 1979) is a collection of physical, chemical, and toxicological data on almost 13,000 common industrial and laboratory materials. The data deal primarily with the hazards posed by the materials and include acute and chronic toxic hazard ratings, toxicity figures, a description of toxicology, treatment of poisoning, and storage, handling, and shipping guidelines.

Physical Chemical Properties of Hazardous Waste Constituents (Dawson, English and Petty 1980) is a collection of data on 250 chemicals commonly found in hazardous waste streams. This collection is an excellent reference for predicting the behavior of chemicals following spills. For each chemical, quantitative estimates are included of the relative human health hazard posed by its release to the environment.

The Merck Index (1976) contains general chemical data on almost 10,000 chemical substances. This work contains descriptions of the preparation and chemistry of the various substances, with citations to the original published sources of the data.

Aquatic Fate Process Data for Organic Priority Pollutants (Mabey et al, 1982) this report includes physical transport, and transformation data for 114 organic priority pollutants in aqueous solutions, and provides methods of calculating partition coefficients and volatilization rates.

Handbook of Chemical Property Estimation Methods (Lyman et al, 1982) is a collection of estimation methods for several physical and chemical properties of organic chemicals with emphasis on environmental processes; it does not actually contain the data. The handbook includes definitions and principles of the properties, overviews of the available methods, and specific instructions for the use of each one including detailed examples. An appendix of the handbook also contains a listing of selected reference books which contain compilations of many physical/chemical properties of organic chemicals.

Data Bases -

OHM-TADS - The Oil and Hazardous Materials-Technical Assistance Data System contains chemical, physical, and biological data on over 850 hazardous chemicals and industrial materials. OHM-TADS contains data describing physical/chemical properties, toxicity, environmental fate and persistence, and emergency response methods. These data are maintained on computer by EPA and are accessible by remote terminal or by microfiche.

Octanol/Water Partition Coefficient Data Base, a data base containing octanol/water partition coefficients for several thousand chemicals, is maintained by Dr. Corlan Hansch at Pomona College, Pomona, California (714--621-8000 ext. 2225). This is perhaps the most complete source of K_{ow} values currently available. The material in this data base can be purchased in hard copy form, on microfiche, or on magnetic tape.

The Chemical Substances Information Network (CSIN) is a computerized data collection system currently being developed by EPA. Sources for this system will initially include the National Library of Medicine, the Chemical Information System, EPA's Chemicals in Commerce Information System, Bibliographical Retrieval Services, System Development Corporation, and Lockheed's Dialog System.

Table 2.2 summarizes the data available from the major handbooks and data bases notes above.

5. Experts

An additional source of information on compound characteristics lies with experts within the chemical industry, scientific community, and hazardous waste response teams.

The Chemical Manufacturers Association (CMA) Chemical Transportation Emergency Center (CHEMTREC) telephone hotline [(800) 424-9300 or 483-7616 in Washington, DC] maintains a directory of industry experts who can be contacted for information related to emergency response. CHEMTREC can rapidly provide information on approximately 18,000 chemicals and trade-name products.

TABLE 2.2 SUMMARY OF CHEMICAL/PHYSICAL DATA AVAILABLE FROM HANDBOOKS AND DATA BASES

	Handbook or Data Base							
	Chris Manual CG446-1,2 (U.S.C.G. 1974b)	EPA Field Detection Manual (1972)	Versch- ueren 1979	Sax 1979	Dawson English and Petty, 1980	Merck Index Wind- holz (1976)	OHM- TADS	Mabey et al SRI (1982)
Chemical Synonyms	X	X	X	X	X	X	X	X
Molecular Weight	X		X	X	X	X		X
Solubility in Water	X		X		X	X	X	X
Vapor Pressure	X		X	X	X		X	X
Boiling Point	X		X	X		X	X	X
Melting Point	X		X	X		X	X	X
Liquid Specific Gravity	X			X	X	X	X	
Vapor Specific Gravity	X		X	X	X			
Saturated Vapor Concentration			X					
Observable Characteris- tics	X	X	X	X		X	X	
Odor Threshold	X		X	X		X		
Sampling and Analysis Methods		X	X				X	
Chemical Reactivity	X					X		
Reactions in Water	X	X	X		X			X
Reactions in Air			X					
Biodegradation Rate Constant			X		X			X
BOD	X		X		X		X	
Hydrolysis Rate Constant				X				X
Photolysis Rate Constant					` X			X
Bioconcentration Factor			X		X			X
Kow					X			X
Kd					X			
Koc					X			X
Number of Chemicals	900	329	1,000	13,000	250	10,000	850	114

Source: after Battelle PNL, 1982a

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Other contacts can be found within local universities, technical assistance teams (TAT) and regional response teams (RRT). Directories of possible contacts are also available through trade organizations and professional societies.

2.4.2 Sources of Site Characterization Information

Site characterization data by its very nature will be much more site and region specific than compound characteristics. Consequently, pre-emergency collection of relevant meteorologic, soils, geologic, and topographic data is especially important. Also, prior hydrologic and hydrogeologic studies of the region may provide a wealth of information. However, regional data must be examined to insure it is representative of site-specific conditions at the emergency response site.

In an emergency response situation, data on site characteristics should be sought from six major sources:

1) Prior Studies

2) Textbooks

3) Well Owners

4) Records

5) Experts

6) Onsite Observations

Textbooks, regional studies, and lists of consultants should be in the hands of the emergency response team before they reach the spill site. It will probably be necessary to refer to many of these data sources at each site, since the required information is seldom found in a single source.

1. Prior Studies

Federal, state, and local government agencies may have performed detailed soils, geologic, water supply, or water quality studies in the area of the site. These prior studies are valuable sources of data on site characteristics. An emergency response team should contact the U.S. Geological Survey, the state geological survey, the local health department and water district, and the local engineering department as a start in the search for prior technical reports. It is expected that many of the site properties might be available in detailed prior investigations. Appendix A of the EPA manual for ground-water/subsurface investigations at hazardous waste sites (EPA, 1981) summarizes an extensive list of contacts and information sources.

2. Textbooks

For some of the geologic and soils properties required in a rapid assessment, tables in geology or ground-water textbooks provide a readily available data source. Ranges of hydraulic conductivity,

bulk density, and porosity should be correlated with types of materials in most texts.

3. Well Owners

Owners of nearby wells may be able to provide information on the aquifer thickness (based on perforated interval of well log), the depth to ground water, the hydraulic gradient in the area, and the nature of the water-bearing strata. Well locations and property boundaries should be sought in assessing the hazards of the spill, thus, conversations with well owners are recommended to search for possible data and sources, such as the drilling company or drillers familiar with the area.

4. Records

To determine the age of the site, records of waste disposal operations or property ownership should be consulted. Waste manifests, describing shipments to the site, may prove useful, but have only recently been required.

5. Experts

In describing the ground water and unsaturated zone of the site, local geologists, water resources engineers, county officials, and university professors will be of assistance. Without detailed prior studies, the estimation of many of the required parameters should be guided by as much expert advice as can be gathered. Local agencies can also aid in locating wells and property boundaries in the site area.

6. Onsite Observations

Wells, topography, property lines, and stream locations should be verified by field reconnaissance at the site.

The major factor which will determine the success and accuracy of the site characterization is the availability of soils/geologic data from previous investigations. Without existing knowledge of subsurface characteristics such as predominant composition and thickness of unsaturated and saturated layers, evaluation of many site parameters will be largely conjecture. It is not likely that field testing will be able to provide adequate geologic data within the time frame of an emergency response assessment. When subsurface material composition is known, many site characteristics including porosity, bulk density, hydraulic conductivity, dispersion, and chemical characteristics can be estimated with reasonable accuracy in some cases (see Section 4). Values for these media-related parameters can be combined with macrogeologic data from reports or regional experts to estimate contaminant transport rates. If available, additional localized

structural and geologic data which identify nonhomogeneity of the subsurface
materials can be used to adjust and/or interpret quantitative estimates of
contaminant transport, which assume media homogeneity. Thus, the ultimate
accuracy of any estimate of contaminant transport will be largely dependent
on the amount of specific localized information available for the emergency
response site.

SECTION 3

RAPID ASSESSMENT NOMOGRAPH AND ITS USE

The quantitative, graphical procedures for contaminant fate and movement in both the unsaturated and saturated zones are presented in this section. A single nomograph was developed for predicting contaminant movement in both soil zones to provide a comprehensive, integrated methodology for use under emergency response conditions. Graphical procedures were selected so as not to require prior experience with computers or programmable calculators by emergency personnel. However, analogous techniques for both the unsaturated and saturated soil zones have been programmed on hand-held calculators providing greater flexibility for assessments (see Pettyjohn et al, (1982) for ground-water programs). With the rapid advances in personal computers and programmable calculators, as emergency response teams acquire the necessary capabilities the techniques described herein can be easily computerized for their use.

Section 3.1 describes in detail the development of the assessment nomograph and Section 3.2 describes its general use, while Section 3.3 describes procedures for linked unsaturated-saturated zone assessments. Finally, Section 3.4 discusses the assumptions and limitations of the technique so that the user can effectively assess the accuracy of predicted concentrations for the specific emergency response situation.

3.1 DEVELOPMENT OF THE ASSESSMENT NOMOGRAPH

This section describes the nomograph developed for assessment of potential ground-water contamination to predict contaminant movement based on input parameters for contaminant and site characteristics.

The background and basis for the methodology is presented, including a discussion of the convective-dispersive transport equation for porous media, the types of pollutant source inputs usually encountered in an emergency response situation (i.e. continuous and pulse inputs) and the corresponding analytical solutions for each input condition. The parameters required to perform an assessment are listed and discussed, followed by the description of the assessment nomograph and its usage. This nomograph is actually a graphical solution of the transport equation and is the heart of the rapid assessment methodology. The same nomograph is used for both zones assuming only vertical transport in the unsaturated zone and only horizontal (or longitudinal) transport in the aquifer (saturated zone). However, the input parameters are evaluated differently for each zone, as will be discussed in Section 4.

3.1.1 Contaminant Fate and Transport in Soils

Movement of contaminants in the soil (saturated or unsaturated) can be described by the following equation (Van Genuchten and Alves, 1982)

$$\frac{\partial c}{\partial t} = D* \frac{\partial c^2}{\partial x^2} - V* \frac{\partial c}{\partial x} - k*C \qquad (3.1)$$

where
C	=	solution concentration (mg/l)
D*	=	D/R
V*	=	V/R
k*	=	k/R
R	=	$1 + \frac{B}{N} K_d$ = retardation factor (dimensionless)
D	=	dispersion coefficient (cm^2/day)
V	=	average interstitial pore-water velocity (cm/day)
k	=	degradation rate coefficient (day^{-1})
B	=	bulk density (g/cm^3)
N	=	θ, volumetric water content (dimensionless), for unsaturated zone
		n_e, effective porosity (dimensionless), for saturated zone
K_d	=	partition coefficient (ml/g)

Equation 3.1 states that the change in contaminant concentration with time at any distance, (X) is equal to the algebraic sum of the dispersive transport (1st term to right of equal sign), the convective transport (2nd term) and the degradation or decay of the compound (3rd term). Van Genuchten and Alves (1982) note that various modified forms of this same basic equation have been used for a wide range of contaminant transport problems in soil science, chemical and environmental engineering, and water resources.

Equation 3.1 considers only one-dimensional transport of contaminants and is applicable under steady, uniform flow conditions, i.e. velocity, V, is constant with space and time. This equation considers dispersion, advection, equilibrium adsorption (linear isotherm), and degradation/decay (first-order kinetics). Analytical solutions to the transport equation have been developed for both continuous (step function) and pulsed inputs of contaminants as boundary conditions. A step function implies the input of a

constant concentration contaminant for an <u>infinite</u> amount of time, while a pulse load is a constant concentration input for a <u>finite</u> amount of time. Clearly, the terms infinite and finite are relative to the time frame of the analysis.

When the pollutant source is applied as a step function (continuously) with the following boundary conditions:

$$C \ (x,o) = 0 \tag{3.2}$$
$$C \ (o,t) = C_o$$

$$\frac{dc}{dx} \ (\infty, \ t) = 0$$

the analytical solution, as given by Cho (1971), Misra (1974), van Genuchten (1982) and Rao (1982), can be expressed as:

$$\frac{C(x,t)}{C_o} = \frac{1}{2} \left[\exp(A_1) \ \mathrm{erfc}(A_2) + \exp(B_1) \ \mathrm{efrc}(B_2) \right] = P(x,t) \tag{3.3}$$

where

$$A_1 = \frac{x}{2D^*} (V^* - \sqrt{V^{*2}+4D^*k^*} \ ) \qquad B_1 = \frac{x}{2D^*} (V^* + \sqrt{V^{*2}+4D^*k^*} \ )$$

$$\tag{3.4}$$

$$A_2 = \frac{x-t\sqrt{V^{*2}+4D^*k^*} \ )}{\sqrt{4D^*t}} \qquad B_2 = \frac{x+t\sqrt{V^{*2}+4D^*k^*} \ )}{\sqrt{4D^*t}}$$

(NOTE: Exp(A_1) denotes the exponential of A_1, i.e., e^{A_1}, while erfc (A_2) represents the "complementary error function" of A_2, a function commonly used in applied mathematics. Erfc(A_2) produces values between 0.0 and 2.0 (Abramowitz and Stegun, 1972)).

The boundary conditions shown in Equation 3.2 indicate that (1) no contaminant is present in the soil prior to input from the source, (2) the input concentration at the surface is constant at C_o, and (3) a semi-infinite column is assumed with a zero concentration gradient at the bottom. This last boundary condition is often assumed to allow development of the analytical solution; van Genuchten and Alves (1982) indicate that this assumption has a relatively small influence on the accuracy of the solution in most circumstances when applied to well-defined finite systems.

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Note that for large values of x and/or t, the second term within the brackets in Equation 3.3 can be neglected (i.e., erfc(B_2) approaches zero) and produces the following:

$$\frac{C(x,t)}{C_o} = \frac{1}{2} [\exp(A_1) \; erfc(A_2)] \tag{3.5}$$

The validity of Equation 3.5 depends on the values of the parameters and variables that define A_1 and A_2. Moreover, Equation 3.5 is comprised of two terms: $\exp(A_1)$ is time-independent and represents the eventual steady-state concentration at x, while $erfc(A_2)$ is time-dependent and corrects for the moving pollutant front (Rao, 1982). Thus, the steady-state condition, where C/C_o is constant and $erfc(A_2) = 2$, simplifies Equation 3.5 to

$$\frac{C(x)}{C_o} = \exp(A_1) \tag{3.6}$$

Under the appropriate conditions stated above, these equations can greatly simplify calculations of contaminant concentrations.

When the pollutant source is applied as a pulse with a pulse duration, t_o, and boundary conditions as shown below:

$$C(x,o) = 0$$
$$C(o,t) = \begin{cases} Co, & o \leq t \leq to \\ 0 & t > to \end{cases} \tag{3.7}$$
$$C(oo,t) = 0$$

the analytical solution, as given by van Genuchten and Alves (1982), and Rao, (1982), can be expressed as:

$$\frac{C(x,t)}{C_o} = P(x,t) \qquad 0 \leq t \leq t_o$$

$$\tag{3.8}$$

$$\frac{C(x,t)}{C_o} = P(x,t) - P(x,t-t_o) \qquad t > t_o$$

where P(x,t) is as defined in Equation 3.3.

Comparing Equations 3.8 and 3.3 shows that the analytical solution to the pulse boundary condition is the result of subtracting the solutions to two continuous inputs lagged by the pulse duration, t_o. This is further explained below.

3.1.2 Continuous and Pulse Contaminant Inputs and Associated Responses

The rapid assessment procedures discussed in this section are directed to two types of contaminant releases found in most emergency situations: continuous and pulse. As noted above, continuous release (or continuous input to the zone) implies the input of a constant source concentration of contaminant to the soil profile for an extended amount of time. This

pollutant source could be an uncontrolled hazardous waste site, an abandoned dump site, a waste lagoon, a leaking chemical/waste container, etc. A pulse input is the application of a constant source concentration for a short time period relative to the time frame of the analysis. In this case, the pollutant source could be a surface spill or a short-term leak from a storage tank. The assessment methodology can be used to predict movement of contaminants in the subsurface resulting from either one of these release situations under emergency response conditions.

Movement of contaminants in the subsurface zones can be expressed by either profile responses or time responses resulting from continuous or pulse inputs. Profile responses are plots of pollutant concentration with distance, x, at various defined times, t. Time responses are plots of concentration changes with time, t, at certain specific locations x. For the unsaturated zone, the distance measure will be the vertical soil depth or depth to ground water; for the saturated zone, the down-gradient horizontal distance to a specific point (e.g., well, stream) will be of interest.

Figure 3.1 graphically illustrates time responses (i.e. C/Co vs t) at a chosen soil depth or distance (x=L) resulting from both continuous and pulse contaminant inputs from the source (x=0). Note that the figure is designed to show that the superposition of two continuous input functions and their associated responses (Figure 3.1a and 3.1b), produces a pulse input and its response (Figure 3.1c). In effect, the continuous input starting at time t_2 is subtracted from the continuous input starting at time t_1; the result is an input pulse of duration t_0 (i.e. $t_2 - t_1$). Similarly, at the point x=L, superposition of the two continuous response functions results in the response function produced by the pulse input. This concept is the basis for the analytical solution for the pulse boundary condition given in Equation 3.8.

Figure 3.2 shows profile and time responses for both the continuous and pulse type releases expected in emergency situations. Specific assessments may involve evaluation of concentrations at many different x and t values.

When profiles are desirable, concentrations must be evaluated at specific times for different values of x; when time responses are needed, concentrations will be estimated for different values of t, for defined soil depths or down-gradient locations. As noted above, for most unsaturated zone assessments, users will be concerned with the concentration and time of arrival of contaminants at the ground-water table. Thus, time responses for an x value equal to the depth to ground water will be commonly calculated. For ground-water (saturated zone) assessments, the horizontal distance in the direction of ground-water flow to a potential impact point is often used.

3.1.3 Required Parameters

In order to predict contaminant movement in soils and ground water, parameters regarding transport and pollutant fate, and boundary or source conditions of an emergency situation must be evaluated. These parameters are listed in Table 3.1, along with their symbols and recommended units.

TABLE 3.1 REQUIRED PARAMETERS FOR RAPID ASSESSMENT PROCEDURES

Parameter/Boundary Condition	Symbol	Recommended Unit
Source Concentration	C_o	mg/l
Interstitial Pore Water Velocity	V	cm/day
Dispersion Coefficient	D	cm^2/day
Degradation/Decay Rate Parameter	k	day^{-1}
Retardation Factor (function of following characteristics)	$R = 1 + \dfrac{B\,K_d}{\theta}$	dimensionless
Partition (Adsorption) Coefficient	K_d	ml/g
Soil Bulk Density	B	g/cm^3
Volumetric Water Content*	θ	dimensionless
Pulse Duration (Pulse input only)	t_o	day

* - For saturated zone assessments, the volumetric water content is equal to the effective porosity, n_e.

C/C_0 C/C_0

(a) Continuous Input, beginning at t_1, and Associated Time Response

C/C_0 C/C_0

(b) Continuous Input, beginning at t_2, and Associated Time Response

C/C_0 C/C_0

(c) Pulse Input of Duration t_o, and Associated Time Response
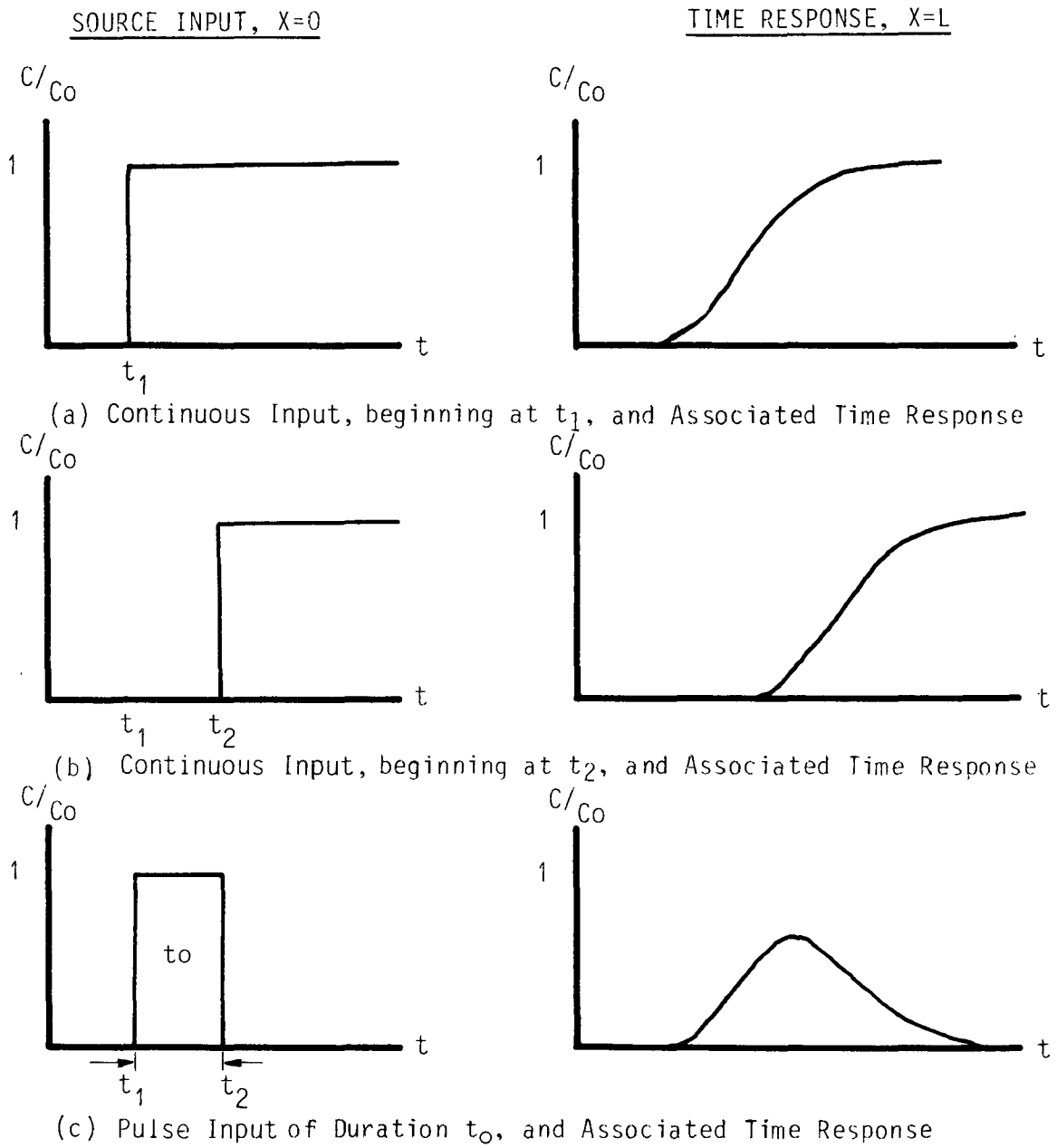
Figure 3.1   Continuous vs. Pulse Contaminant Inputs
and Associated Responses

Profile Response   Time Response

(a)   For Continuous Input

Profile Response   Time Response
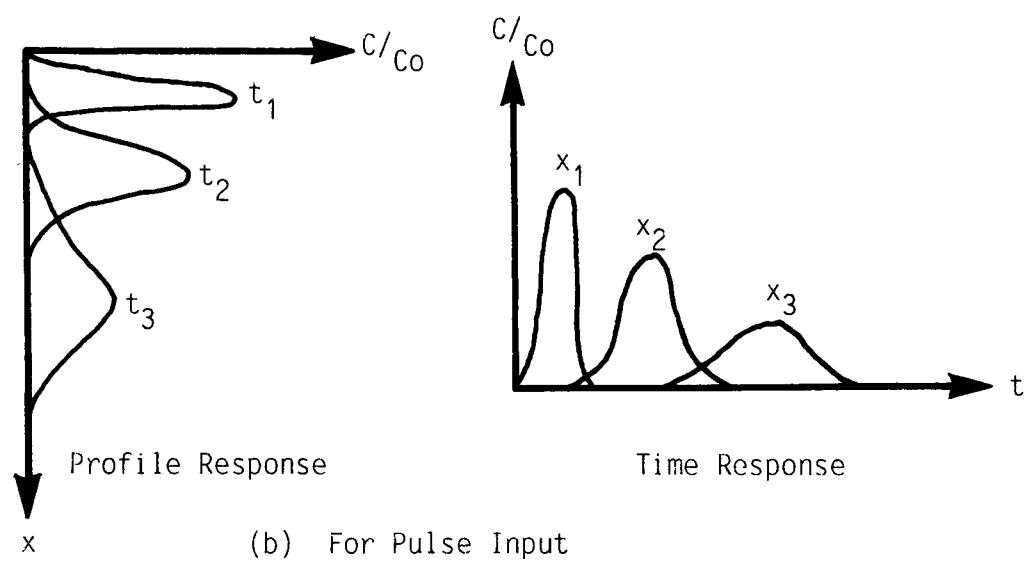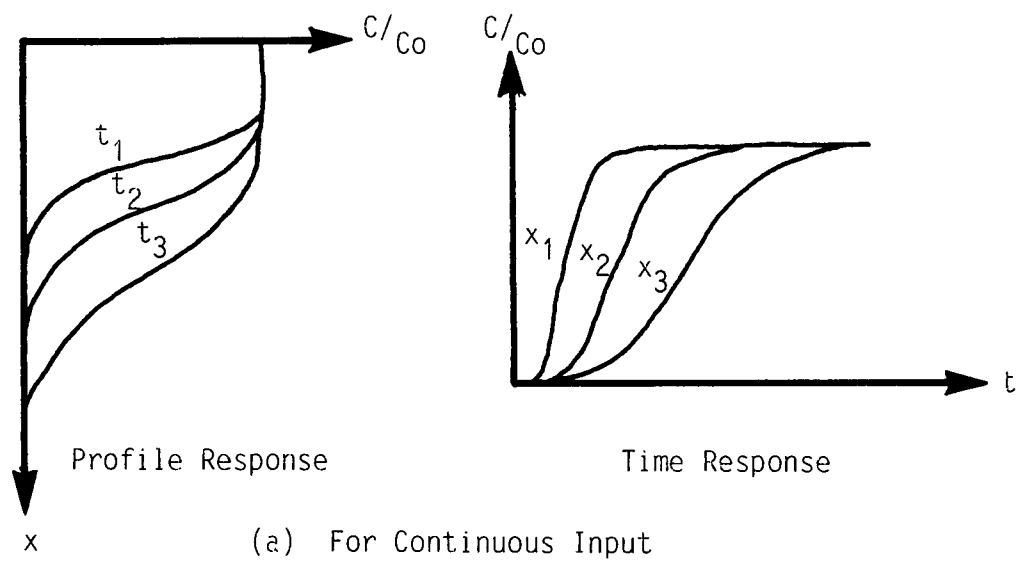
(b)   For Pulse Input

Figure 3.2   Contaminant Movement Expressed by Profile and
Time Response to Continuous and Pulse Inputs

Transport parameters include the interstitial pore water velocity (V) and dispersion coefficient, (D). Pollutant fate parameters include the degradation/decay coefficient (k) and retardation factor, (R). Retardation is primarily a function of the adsorption process which is characterized by a linear, equilibrium partition coefficient (K_d) representing the ratio of adsorbed and solution contaminant concentrations. This partition coefficient, along with soil bulk density (B) and volumetric water content (θ), are used to calculate the retardation factor. Retardation is important in contaminant transport in the unsaturated zone because it affects pollutant movement by modifying the convective, dispersive and degradation terms in the transport equation (Equation 3.1) as follows:

$$V* = V/R$$
$$D* = D/R \hspace{3cm} (3.9)$$
$$k* = k/R$$

Boundary conditions of a waste or spill situation are characterized by the contaminant concentration, Co, of the pollutant source. For a release situation characterized as a pulse input, the pulse duration, (t_o) must also be specified.

Section 4.2 includes further discussion of the parameters listed in Table 3.1 and provides guidelines for estimating their values.

3.2 THE NOMOGRAPH AND HOW TO USE IT

The assessment nomograph was developed to facilitate computation of the analytical solution to the transport equation for emergency situations which can be characterized as continuous (step function) input. However, through superposition (as discussed above) the same nomograph can be used for waste/spill conditions characterized as pulse input. The nomograph (Figure 3.3) predicts contaminant concentration as functions of both time and location in either the unsaturated or saturated zone. Separate computations, parameter estimates, and use of the nomograph is required for each zone. The prediction requires evaluation of four dimensionless input values - A_1, A_2, B_1, and B_2 - and subsequent evaluation of the result, C/Co, according to Equation 3.1 through use of the nomograph.

Direct computation of C/Co is quite cumbersome; in addition to parameter calculations, it involves evaluation of both the exponential and complementary error functions, and subsequent arithmetic operations. The nomograph facilitates these computations.

As shown in Figure 3.3; the nomograph consists of two groups of curves joined in the center by three vertical axes. Both curve groups have two axes, vertical and horizontal. The horizontal axis to the left is for entry of A_1 and to the right entry of B_1. Both axes are scaled to provide evaluation of their corresponding exponential functional values (exp [A_1] and exp [B_1], respectively). The vertical axis to the left is for entry of A_2 and to the right, entry of B_2. Both axes are scaled to provide
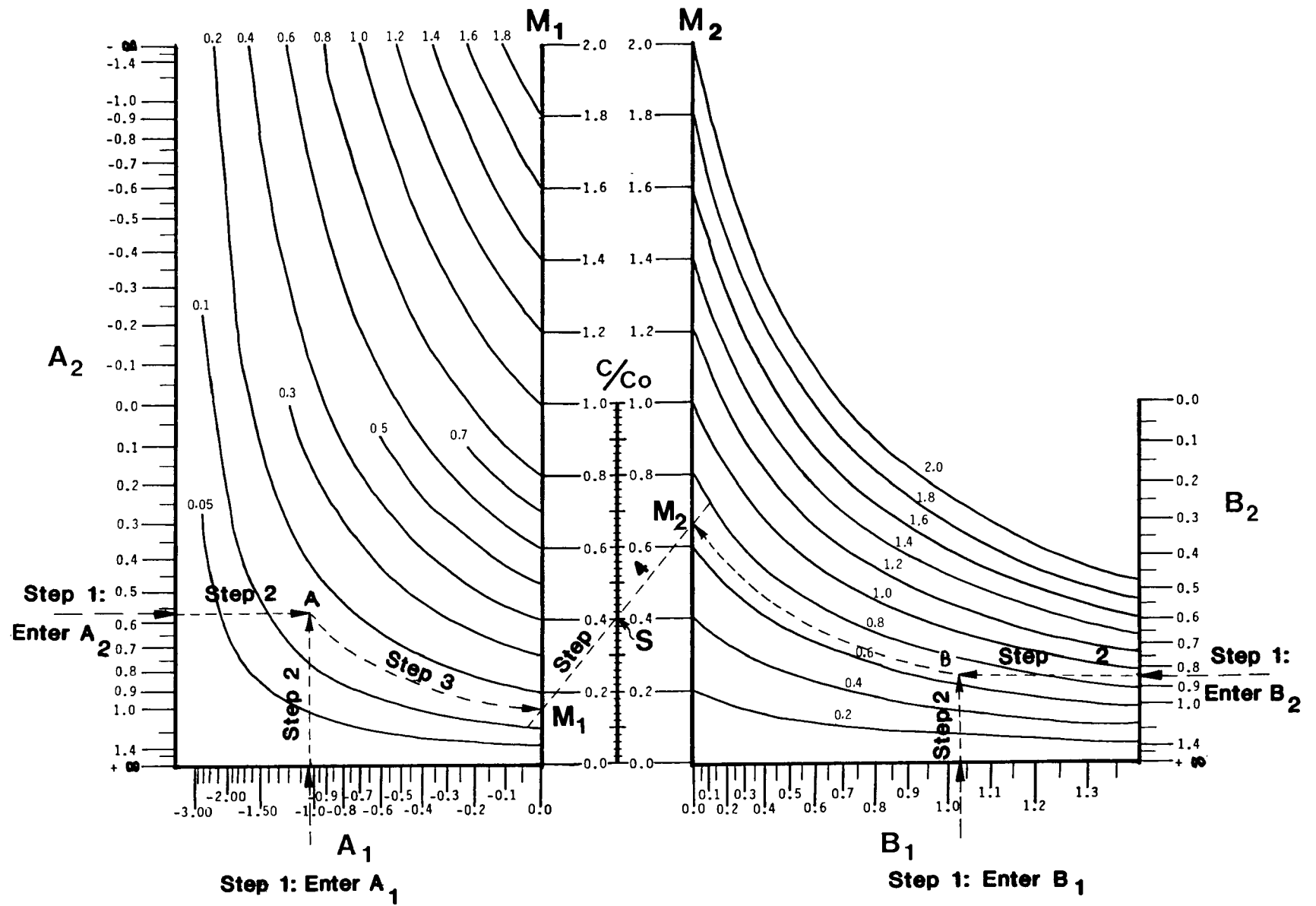
Figure 3.3   The Rapid Assessment Nomograph and Procedures for its Use

evaluation of their corresponding complementary error functional values (erfc [A_2] and erfc [B_2], respectively): the intersection of A_1 and A_2, and B_1 and B_2 (points A and B in Figure 3.3) represents the product of the axes, i.e. exp(A_1) times erfc(A_2). The two groups of curves represent points of equal multiplicands. The solution, C/Co, is located in the middle as represented by the center axis. The remaining two axes on both sides of the solution are multiplicands of the exponential and the erfc values. The curves represent points of equal multiplicands.

Step-by-step procedures are outlined below to demonstrate use of the nomograph.

Step 1: A_1, A_2, B_1, and B_2, must first be calculated. This can be done by inputting selected parameter values into Equation 3.4.

Step 2: Once A_1, A_2, B_1, and B_2 are calculated, C/Co can be obtained from the nomograph (Figure 3.3). Start by entering values of A_1 and A_2 to the left group curves and B_1 and B_2 to the right. As represented by the dotted lines labeled "step 2," the entering lines join at points "A" and "B" respectively.

Step 3: Then draw curves "AM_1" and "BM_2" by following the patterns in each respective curve group. As shown in Figure 3.3 these curves intersect the center axes at points "M_1" and "M_2".

Step 4: The solution, C/Co, can finally be obtained by drawing a straight line connecting points "M_1" and "M_2". The solution is found at the point where line "M_1M_2" intersects the solution line, C/Co. In this example, the solution is located at point "S".

The precision of a nomograph is determined both by its size and the divisions of the axes. Large nomographs with fine divisions, in general, will allow greater precision. The full scale nomograph provided in this section (Figure 3.3) is precise enough for use with a continuous input or a long pulse input situation. However, higher precision is needed for conditions with a short contaminant pulse, especially for low C/Co values. For this reason, a nomograph with an enlarged scale (Figure 3.4) is provided to magnify the lower portion of the full nomograph, for C/Co values less than 0.4. For ease of use, enlarged foldout versions of both the full-scale and expanded-scale nomographs are provided in Appendix C.

To organize application procedures and provide a record of calculations and predicted concentrations, worksheets are provided to complement the nomograph for predicting contaminant concentrations for different values of x and t. Step-by-step procedures in applying these worksheets in emergency assessments are discussed below separately for the two contaminant input situations.

Worksheet Procedures for Continuous Input Assessment

Step 1:   Evaluate "required parameters" and enter values in Table 3.2.
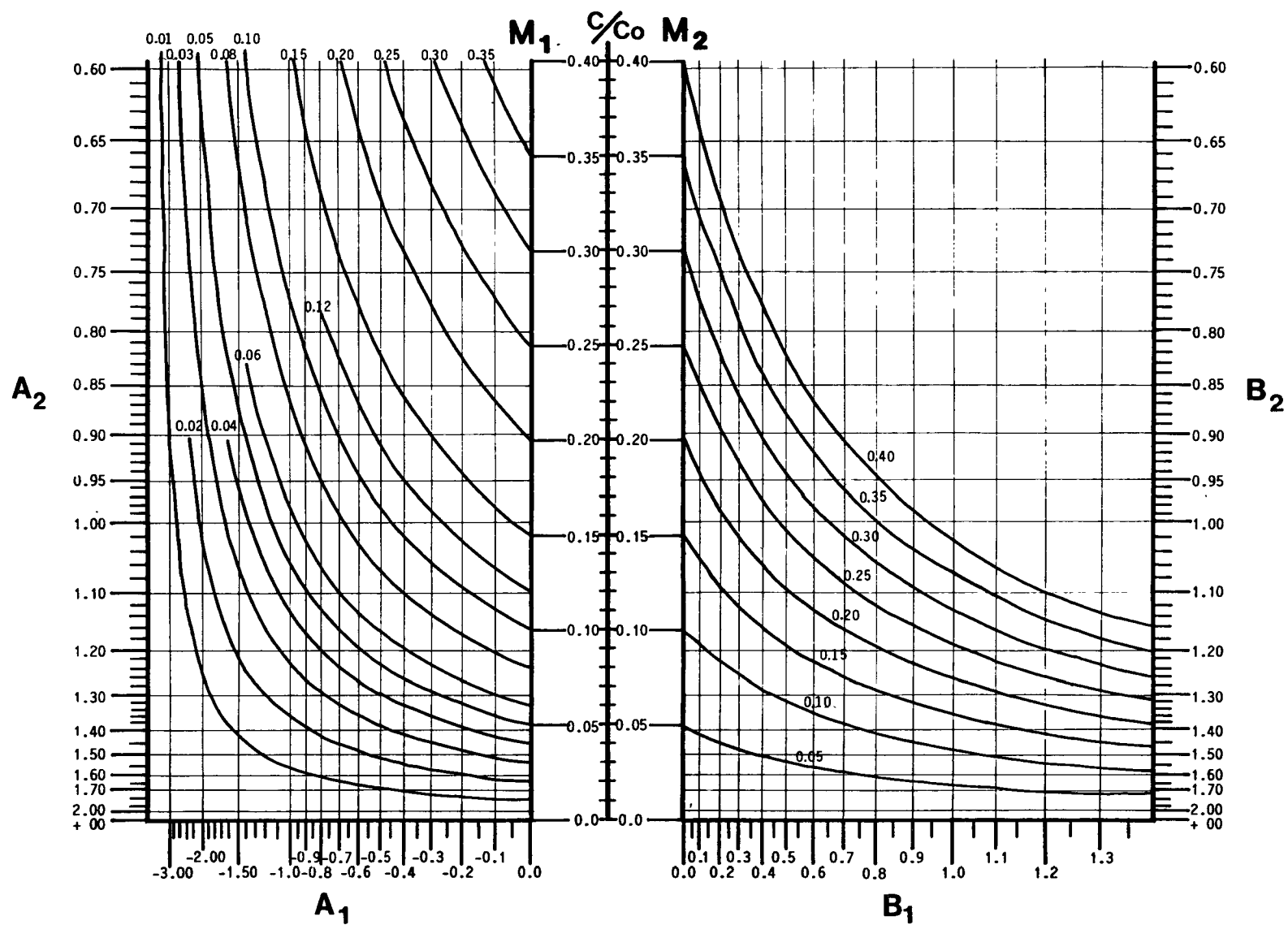
Figure 3.4   Rapid Assessment Nomograph - - - Enlarged Scale, $C/C_o < 0.4$.

Table 3.2

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED _____

SATURATED _____

Site: _____ Date of Incident: _____

Location: _____

On Site Coordinator: _____ Agency: _____

Scientific Support
Coordinator: _____ Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS: **DATA SOURCES / COMMENTS**

Co = _____ _____

V = _____ _____

D = _____ _____

k = _____ _____

R = $1 + \dfrac{B}{\theta} K_d$ = _____ _____

K_d = _____ _____

B = _____ _____

θ = _____ _____

PRELIMINARY CALCULATIONS:

1. $V^* = V/R$ = _____ 3. $k^* = k/R$ = _____

2. $D^* = D/R$ = _____ 4. $\sqrt{V^{*2} + 4D^*k^*}$ = _____

5	6	7	8	9				10	11	12
				See Footnote # 2				From Nomograph[3]		
x	t	$x/2D^*$	$\sqrt{4D^*t}$	A_1	A_2	B_1	B_2	M_1	M_2	C/Co	C

Table 3.2

NOMOGRAPH WORKSHEET (con't.)

ZONE: UNSATURATED _____

SATURATED _____

5	6	7	8	9				10		11	12
x	t	$x/2D*$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]			C
				A_1	A_2	B_1	B_2	M_1	M_2	C/Co	

Footnotes:

1. Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. $A_1 = \text{Col.7} \times (\text{Item 1} - \text{Item 4}) = \dfrac{x}{2D*}(V* - \sqrt{V*^2 + 4D*k*})$

   $A_2 = [\text{Col.5} - \text{Col.6} \times \text{Item 4}] / \text{Col.8} = \dfrac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

   $B_1 = \text{Col.7} \times (\text{Item 1} + \text{Item 4}) = \dfrac{x}{2D*}(V* + \sqrt{V*^2 + 4D*k*})$

   $B_2 = [\text{Col.5} + (\text{Col.6} \times \text{Item 4})] / \text{Col.8} = \dfrac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

3. Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

Step 2:   Perform preliminary calculations.

Step 3:   Enter values of x and t.
            o To obtain a profile response, enter different values of x
               for a selected time, t.

            o To obtain a time response, enter different values of t for a
               selected location, x.

Step 4:   Perform calculation and apply nomographs, to evaluate C/Co and
            C as instructed in the worksheet.

Step 5:   Go back to Step 3 for further evaluation, if necessary.

Worksheet Procedures for Pulse Input Assessment

As mentioned earlier in Section 3.1.2, the analytical solution for a pulse
contaminant input results from the superposition of solutions for two separate
continuous input functions lagged by the pulse duration. Since the assessment
requires substracting two continuous input response (i.e. C/Co) values, a
supplementary worksheet (Table 3.3) is provided.

Step-by-step procedures for the pulse input situation are provided below:

Step 1:   Evaluate "required parameters," enter pulse duration (t_o) and
            source concentration (Co) in Table 3.3 and other parameter
            values in Table 3.2.

Step 2:   Perform preliminary calculations in Table 3.2.

Step 3:   Enter values of x and t in Table 3.3, and in Table 3.2 for
            continuous input assessment.

            o To obtain a profile response, enter different values of x
               for a selected time, t, in both Tables

            o To obtain a time response, enter different values of t for a
               selected location, x, in both Tables

Step 4:   Perform continuous input assessment using work sheet Table 3.2
            and enter result C/Co, in column 11 of Table 3.2 and column 4
            of Table 3.3.

Step 5:   Evaluate ($t-t_o$) in Table 3.3. If $t > t_o$, go to Step 6.
            Otherwise, pulse concentration (Column 6) equals the continuous
            input concentration (Column 4). Go to step 8.

Step 6:   Evaluate C/Co at ($t - t_o$) using worksheet Table 3.2 and enter
            result in column 5 of Table 3.3.

Step 7:   Subtract column 5 from column 4 and enter result in column 6.

Table 3.3   Sheet _____ of _____

SUPPLEMENTARY WORKSHEET FOR PULSE INPUT ASSESSMENT

ZONE: UNSATURATED _____

to = _____ ,   Co = _____   **SATURATED** _____

1	2	3	CONTINUOUS INPUT ASSESSMENT (From Worksheet)		PULSE ASSESSMENT	
					Col.4, $t \leq$ to Col.4-5, $t >$ to	Co X $\frac{Col.}{6}$
1	2	3	4	5	6	7
x	t	t - to	C/C_o (t)	C/C_o (t - to)	C/C_o (t)	C

Step 8:   Multiply column 6 by Co and enter result in column 7 of Table
           3.3.

Step 9:   Go back to Step 3 for further evaluation if necessary.

Detailed examples demonstrating the use of the nomograph and the worksheets
for both continuous and pulse inputs are provided in Section 5. The user is
encouraged to work through these examples and procedures to become familiar
with them prior to an emergency response situation.

3.3 LINKAGE OF UNSATURATED AND SATURATED ZONE ASSESSMENTS

Since the assessment nomograph can be applied to both the unsaturated and
saturated zones individually, linkage procedures are required for situations
where an assessment of contaminant movement through both saturated and
unsaturated media is needed. The linkage procedures require the following two
steps:

1.   Approximation of the time-varying concentrations leaving the
      unsaturated zone by either a continuous step function or pulse input.

2.   Estimation of C_O (i.e., source concentration) for the saturated
      zone assessment based on Step 1 (above), recharge from the waste
      site, and ground-water flow.

Figure 3.5 shows typical time responses for concentrations reaching ground
water as estimated by an unsaturated zone assessment for both continuous and
step function inputs; the dashed lines show the approximations needed to
convert the time responses into continuous or pulse inputs for applying the
nomograph to the saturated zone. The approximations in Figure 3.5 are
designed so that the area under the dashed line is approximately equal to the
area under the associated time response curve. This ensures that the
contaminant mass entering ground water is the same for both the time response
and its approximation.

Since the arrival time of a contaminant at a particular point in the aquifer
is often the primary reason for a saturated zone assessment, users should
evaluate the sensitivity of these arrival times to the starting time of the
input approximation. For example, in Figure 3.5 the starting dates for the
step function and pulse input approximation are day 15 and day 10,
respectively; varying these starting dates by 2 to 3 days would help to
evaluate the impact of the approximation on the contaminant arrival time at
the point of concern.

The second step in the linkage procedure is to determine the value of C_O,
the source concentration, to use in the saturated zone assessment. Unless the
waste/spill site is adjacent to a well and/or the ground-water table itself is
the impact point of concern, dilution and mixing in the aquifer must be
considered in estimating C_O for the saturated zone assessment. The
following equation should be used to estimate C_O for the saturated zone:

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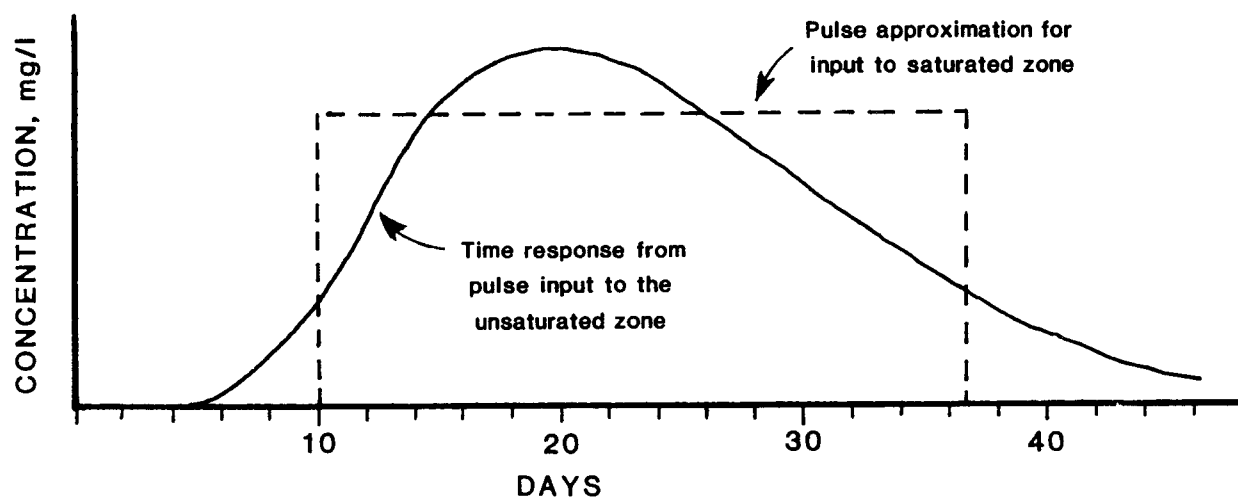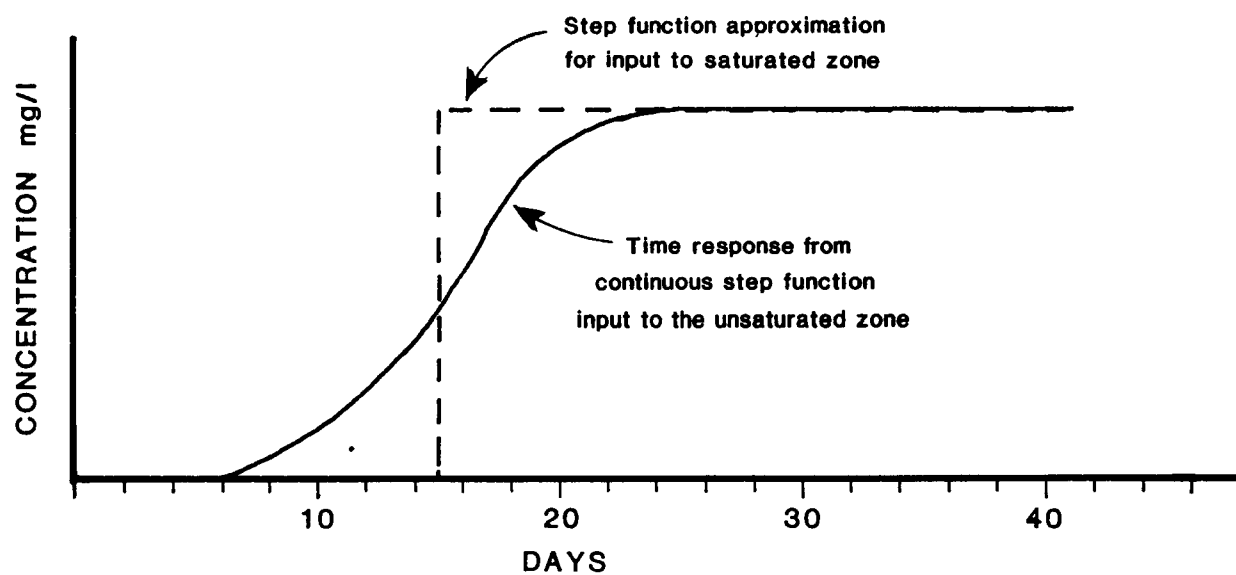
Figure 3.5   Time Responses From The Unsaturated Zone and Approximations
For Input To The Saturated Zone

$$C_o = \frac{C_u qL}{V_d m} \qquad (3.10)$$

where C_o = source concentration for saturated zone, mg/l

C_u = maximum step function or pulse concentration from the unsaturated zone, mg/l

q = recharge rate from the site, cm/yr

L = width of leachate plume at the water table, m

V_d = ground-water (Darcy) velocity, cm/yr

m = effective aquifer thickness or zone of mixing, m

Figure 3.6 schematically illustrates the linkage and underlying assumptions in Equation 3.10, which considers dilution of the contaminant load by recharge from the site and ground-water flow. The dilution terms (i.e., qL and V_dm) in the equation are written as a velocity times a distance since the representation is a vertical plane with a unit width, which drops out of the calculation.

Users should note that the q and V_d terms in the equation are bulk or volumetric velocities, i.e., these are not pore-water velocities. Guidelines for estimating q, V_d and m are included in Section 4, L is determined from the dimensions of the waste/spill site, and C_u results from the approximation shown in Figure 3.5. With this information and nomograph parameter estimates for the saturated zone, the user can apply the nomograph to estimate contaminant concentrations in the aquifer.

3.4 ASSUMPTIONS, LIMITATIONS, AND PARAMETER SENSITIVITY

To effectively and intelligently use the rapid assessment procedures described in this manual, the user must understand and appreciate the impact of assumptions and limitations on which the procedures are based, and the relative sensitivity of the required parameters. These two aspects are interrelated; performing sensitivity analyses on certain parameters will allow the user to assess the impact of specific assumptions. Sensitivity analyses were noted in Section 2.2 as a key element in applying the assessment methodology.

3.3.1 Methodology Assumptions

The assumptions on which the assessment nomograph is based are as follows:

1. All soil and aquifer properties are homogeneous and isotropic throughout each zone.

2. Steady, uniform flow occurs only in the vertical direction throughout the unsaturated zone, and only in the horizontal
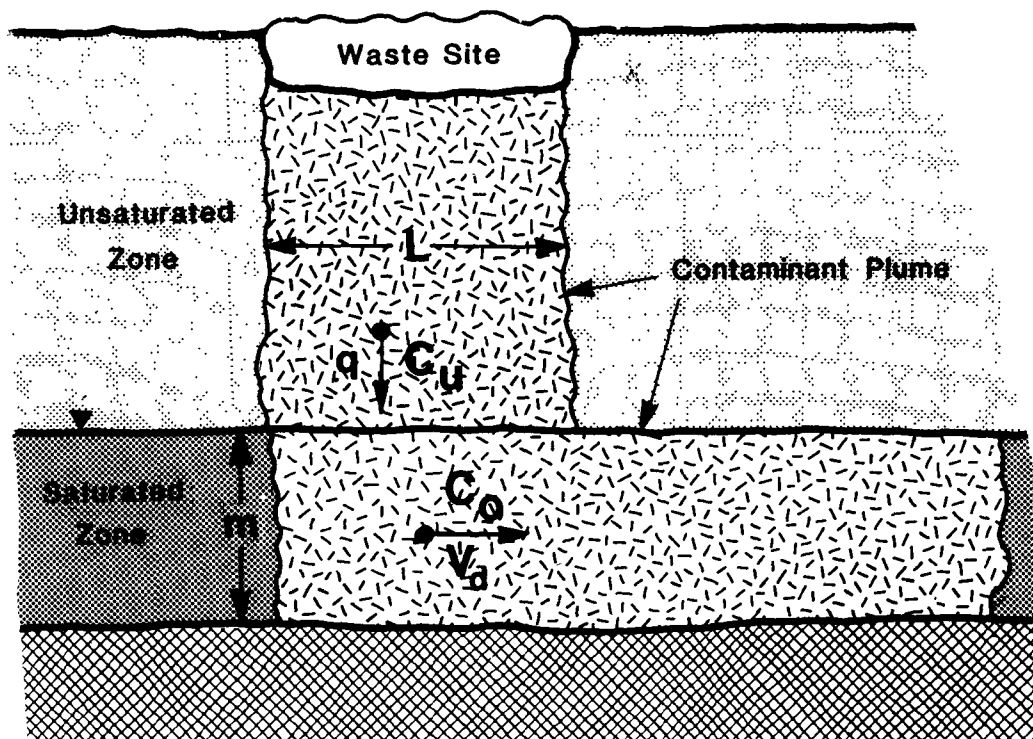
Figure 3.6 Schematic Linkage of Unsaturated and Saturated
Zone Assessments

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(longitudinal) plane in the saturated zone in the direction of ground-water velocity.

3. Contaminant movement is considered only in the vertical direction for the unsaturated zone and horizontal (longitudinal) direction for the saturated zone.

4. All contaminants are water soluble and exist in concentrations that do not significantly affect water movement.

5. No contaminant exists in the soil profile or aquifer prior to release from the source.

6. The contaminant source is applied at a constant concentration continuously; a pulse input can be handled by superposition (Section 3.1).

7. There is no dilution of the plume by recharge outside the source area.

8. The leachate is evenly distributed over the vertical dimension of the saturated zone.

The assumption of homogeneous and isotropic conditions is equally critical in both zones. In many cases, extensive heterogeneities will exist for both soil and aquifer properties, but the emergency response time frame precludes adequate consideration of variations even if they are known to exist. Adjustment of certain parameters may be possible to estimate an "effective" parameter value that partially accounts for property variations. However, conditions involving soil cracks, fractured media, impermeable layers, clay lenses, etc. will require the user to make a qualitative assessment on their potential impact on predicted concentrations.

The assumption of steady, uniform flow is much more critical in the unsaturated zone than in the saturated zone. Pore water velocities are significantly more dynamic and variable in the unsaturated zone since they depend on the percolation flux from rainfall and variable soil moisture conditions, which in turn affect other soil properties. Under-estimation of travel times in the unsaturated zone can occur if mean annual percolation rates are used to estimate movement of the contaminant front during shorter time periods (e.g., months). Ground-water flow velocities are also difficult to estimate, but they are less dynamic than in the unsaturated zone. Consequently, great care is needed in estimating velocities in both zones.

The assumption that contaminants are water-soluble and exist in concentrations that do not impact water movement is relevant to both zones but may be more critical for the unsaturated zone. Surface and unsaturated soils will likely experience higher concentrations than ground water due to accidental spills or releases. Also, the majority of contaminants that reach ground water after traveling through a reasonable depth of unsaturated soil will likely be water soluble. Although water solubility is assumed

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since the contaminant is moving with the water, the same basic form of the transport equation has also been used to assess movement of the soluble portion of oil spills in ground water (Duffy et al, 1980).

The accommodation of contaminant pulse inputs was discussed in Section 3.1 using the principle of superposition. The same principle and procedures are used for both zones to assess plume migration from a pulse input. However, for short pulses and low concentrations the precision of numbers read from the nomograph may be the primary limitation (see discussion below).

3.3.2 Limitations and Parameter Sensitivity

In addition to the assumptions noted above the major limitations of the procedures described herein include the precision with which numbers can be read from the nomograph (an inherent limitation of graphical procedures) and the reliability and accuracy of parameter estimates. As shown on the nomograph, the C/Co values can be read from Figure 3.3 (full-scale) to two decimal digits (i.e. 0.01) and from Figure 3.4 (expanded scales, C/Co < 0.4) to three decimal digits (i.e. 0.001). If greater precision is required, direct calculation of the solution by Equation 3.3 may be needed.

The greatest limitation on predictions will be the accuracy and reliability of the data for estimating parameters. In most emergency situations, specific compound and site data will be difficult to obtain; however, all efforts should be made to acquire the most reliable and site-specific data as possible through the sources and guidelines provided in Section 4. Even with relevant data for parameter estimation, users should perform sensitivity analyses as recommended in Section 2.2 in order to assess the impact of possible parameter variations and methodology assumptions on predicted concentrations.

Pettyjohn et al (1982) have performed sensitivity analyses on the major parameters for an analogous nomograph for the saturated zone only; the user is referred to that source for complete details. Depending on the specific data available for individual parameters, the user should consider assessing the sensitivity of the following parameters which are generally the most sensitive:

    Degradation/decay rate
    Retardation factor
    Pore Water Velocity
    Source Contaminant Concentration
    Effective aquifer thickness (saturated zone only)
    Dispersion coefficient

Degradation/decay and retardation are interrelated since retarding the movement of the contaminant will allow greater time for degradation to occur. Velocity is a sensitive parameter for both zones. Since it is highly variable and can range over orders of magnitude, assessments of its sensitivity in site-specific situations is highly recommended

For the saturated zone, the effective aquifer thickness or zone of mixing represents the degree to which the contaminant is uniformly mixed in the vertical direction. For very shallow aquifers, using the entire thickness may be appropriate. For deep aquifers, mixing zones considerably less than the total may be required. Consequently, the effect of varying mixing depths should be assessed by the user.

Dispersion in ground water can be significant especially at low ground-water velocities. Since the coefficient can vary over a wide range, accurate estimates of expected subsurface conditions can be extremely difficult. Sensitivity should be analyzed.

Source contaminant concentrations may be the most difficult of all data to obtain and/or characterize, especially for landfill, lagoon, or other waste site situations. If a range of possible or probable values can be estimated, the user should definitely evaluate the concentration predictions that would result from the full potential range of source values.

SECTION 4

PARAMETER ESTIMATION GUIDELINES

The most important part of the rapid assessment methodology is estimation of reasonable and valid parameter values for a specific emergency response situation. Section 2.3 described and discussed the critical compound and site characteristics that determine the potential for ground-water contamination at a particular hazardous waste or spill site. This section provides specific guidelines for estimation of the parameter values needed for use of the rapid assessment nomograph described in Section 3. The format of this section is as follows:

Section 4.1 General Parameter Estimation

Section 4.2 Unsaturated Zone Parameter Estimation

Section 4.3 Saturated Zone Parameter Estimation

For each parameter, guidelines are provided, to the extent possible, for calculating the parameter value and estimating the relevant compound and site characteristics on which it depends. Thus, discussions of characteristics are grouped according to the affected parameters. For example, since the retardation factor for organic compounds depends upon organic carbon content, organic carbon partition coefficient, bulk density, and porosity (saturated zone), these characteristics are discussed under the section on estimating the retardation factor. For parameters needed in <u>both</u> the unsaturated and saturated zone assessments, the primary discussion is Section 4.2 (unsaturated) with any adjustments required for the saturated zone in Section 4.3.

Some repetition of information in Section 2.3 (characteristics) and 2.4 (data sources) is included in this section to preclude the need to continuously turn back to the earlier sections and to clarify the presentation. Once the user is familiar with the content of this manual, this section will likely receive the most usage on a continuing basis especially during an emergency response.

The user will note that the following statement is repeated numerous times in this section:

<u>Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.</u>

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This emphasizes the need to search for and use local site-specific information for the parameter being discussed. The statement is repeated to insure that the user is aware of possible errors that can result from the use of general or regional data whenever the parameter must be estimated.

4.1 GENERAL PARAMETER ESTIMATION

This section discusses general characteristics important to assessment procedures in <u>both</u> zones, including identity and concentration of contaminants, nature of the soils and geologic strata, age of the waste/spill site, and depth to ground water. The contaminant concentration is the only characteristic discussed that results in a specific parameter value used in the nomographs. However, the other characteristics are important in applying the assessment procedures, evaluating assumptions, and determining compound/site characteristics.

4.1.1 Identity of Contaminants

Obviously the identity of the contaminants present at the waste/spill site is necessary to evaluate the relevant physical/chemical properties needed for predicting fate and migration. In many cases the identity will have been established by emergency personnel (e.g. at a spill site) or prior analyses (e.g. drinking water problems) in order to determine the need for an emergency ground-water assessment. Identification can be established quickly, on the order of several hours, through the use of records and observable characteristics. Chemical analyses can be used, if necessary, but they require considerably more time, and may need to be limited to qualitative field methods in order to give results within the emergency response 24-hour time frame.

Records provide the most rapid, positive identification of contaminants involved in a hazardous waste accident and should therefore be the focus of the initial efforts at contaminant identification. Shipping papers and transportation labels are now required when transporting hazardous materials. In addition, the Association of American Railroads is developing a computerized tracking system for rapid identification of railcars containing hazardous materials (Guinan, 1980).

The use of records to identify chemicals present at uncontrolled waste sites is much more difficult. Waste manifests, listing each waste shipment received at the facility, are a possible source of data, but these manifests have only recently been required in many cases. Waste site owners and/or companies who have disposed materials at the site may be able to provide some information on the types of contaminants present.

If records are unavailable or incomplete, observable characteristics such as odor, color, density, and reaction should be investigated as clues to the identity of the waste. The following handbooks and data bases (described in section 2.4) provide information to aid in waste identification based on observable characteristics:

1) Field Detection and Damage Assessment Manual for Oil and Hazardous Materials Spills, U.S. EPA, Washington, DC, 1972.

2) U.S. Coast Guard Chemical Hazard Response Information System, Manual CG-446-1, A Condensed Guide to Chemical Hazards, and Manual CG-446-2, Hazardous Chemical Data, Washington, DC, 1974.

3) OHM-TADS Data System, U.S. EPA.

In addition to printed and computerized information on observable characteristics, experts within the chemical industry (Chemical Transportation Emergency Center (CHEMTREC) at (800) 424-9300 or 483-7616), at local universities, and at regional response teams (RRT) can be contacted for assistance.

Field analytical methods will be difficult to apply within an emergency response time frame and should therefore be called upon for compound identification only after first considering records and observable characteristics. The Field Detection and Damage Assessment Manual for Hazardous Spills (EPA 1972), the EPA Field Guide for Scientific Support (Battelle PNL 1982a) and the EPA's OHM-TADS system describe the use of several analytical methods for identifying hazardous chemicals. A variety of chemical products are available for in-field analysis. The application of these analytical methods will require the presence of a skilled technican, experienced in the operation of these instruments.

4.1.2 Contaminant Concentration

The source concentration of the specific contaminant(s) to be analyzed is a required input parameter for both the unsaturated and saturated zone assessments. For the unsaturated zone, the user must specify the concentration of the contaminant available to the soil after deducting potential losses due to volatilization, decay processes, clean-up/removal operations, retention by liners and/or non-leaking drums, etc. In many emergency response situations, the initial contaminant concentration may be the most difficult of all parameters to estimate. A variety of sources of information should be consulted to uncover data specific to the waste site or spill under investigation.

Records and industry experts should be the primary sources contacted initially to uncover concentration data. Although waste disposal site records (if available) and transport manifests do not often contain concentration data, they may identify the general category of the waste/contaminant, the industry or companies that generated the compound, and possible contacts for further information. Also, the procedures and sources used to identify the contaminant (e.g. CHEMTREC, AAR) may also be useful in estimating concentrations. Industry contacts and experts may be able to provide estimates of concentrations at which the chemical is normally transported (i.e. for spills) or resulting from a particular industry or industrial process (i.e. for waste sites).

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Chemical analyses by mobile laboratories or other emergency or field procedures can provide the needed information, and will usually be ordered by the on-scene coordinator once it is determined that a toxic or hazardous compound is involved. However, the results of chemical analyses may not be available within the emergency response time frame, especially if subsurface sampling is required. The above sources should be contacted concurrently while samples are being taken and analyzed in order to expedite obtaining concentration information and performing the assessment procedures.

Lacking any information on the contaminant concentration, we recommend that the user assume the source concentration equal to the water solubility of the contaminant. In most situations this is an appropriate assumption for an initial assessment since movement of the contaminant through the unsaturated zone will occur primarily by the infiltrating water carrying the water soluble portion of the compound. Although retardation and decay processes will subsequently reduce unsaturated zone concentrations, the water solubility is a reasonable estimate of the source contaminant concentration. This assumption has been used by Falco et al (1980) in a screening procedure for assessing potential transport of major solid waste constituents in releases from landfills and lagoons.

Water solubility data for specific compounds and hazardous waste constituents is available in the following data sources:

1) CHRIS Manual CG 446-1,2 U.S. Coast Guard, 1974

2) OHM-TADS, U.S. EPA Data Base

3) Physical Chemical Properties of Hazardous Waste Constituents, U.S. EPA, 1980

4) The Merck Index, Merck and Company, Inc. (Windholz, 1976)

5) Handbook of Environmental Data on Organic Chemicals (Verschueren, 1977)

6) Aquatic Fate Process Data for Organic Priority Pollutants, (Mabey et al 1982)

In addition, Lyman et al (1982) describe a variety of methods of estimating solubility in water and other solvents from data on melting point, structure, octanol-water partition coefficients, activity coefficients, and other compound characteristics.

Alternatively, for compounds that are considered to be a small fraction of the total waste volume at a site, Falco et al (1980) assumed the concentration in the leachate to be the equilibrium concentration resulting from partitioning between the solid and dissolved phases of the waste compound. Thus the source solution concentration could be estimated as follows:

$$C_s = \frac{F}{K_{om}} \qquad\qquad (4.1)$$

where C_s = source solution concentration, mg/l

K_{om} = partition coefficient between organic matter and
solution, 1/mg

F = fraction of solid waste that is the contaminant of
interest

F must be evaluated from records and other information available for the specific waste site, and K_{om} is discussed in Section 4.2.

The user should be aware that for water insoluble or slightly soluble compounds from waste sites or spills, the assumption of using water solubility values could lead to significant errors. This will be especially important for large volume spills of such chemicals where gravity and the mass of the spill are the driving forces for moving the contaminant through the unsaturated zone. (See Section 4.2 for further discussion). The above assumptions and methods of estimating the source concentration should be used only as a last resort when no other data or information is available.

Chemical Loss Mechanisms

In addition to leaching to ground water and chemical decay processes in the soil, chemical losses from the spill site may occur via photochemical decay and volatilization. These processes will help to reduce the contaminant concentration available to move through the soil, and should be considered when estimating this concentration value.

Photolysis rates depend on numerous chemical and environmental factors including the light absorption properties of the chemical, the light transmission characteristics of the chemical (if pure) or its environment (water, soil, etc.), and the available solar radiation of appropriate wave length and intensity. Estimation of the chemical's general photolytic reactivity and the light transmission properties of its environment or solvent will usually be very difficult. Also, most existing models and data (e.g. Smith et al, 1977; Callahan et al, 1979) for predicting photolytic decay in the environment are applicable to atmospheric and aquatic systems. Consequently, the quantitative estimation of attenuation of a chemical concentration by photolysis at a spill site during a 24-hour emergency response period would be impossible. The best we can do is to assess the probability of photolysis being an important loss mechanism and then adjust the assessment results accordingly when photolysis is ignored. The following steps are recommended:

1) Determine whether the chemical is exposed to direct solar radiation. If most of the chemical has percolated into the soil,

photolysis can be neglected; if the chemical is directly exposed, go to step 2.

2) Determine whether the chemical is susceptible to photolysis by consulting with a) industry officials familiar with the specific chemical or b) environmental photolysis reference books and literature (e.g. Callahan et al, 1979; U.V. Atlas of Organic Compounds 1966-1971). This step may be subject to considerable error, however, since the photochemical reactivity of a chemical is determined by its physical state (dissolved, solid, liquid, adsorbed) and environment (solvent, etc.) as well as its molecular structure.

3) If both 1 and 2 above are positive, the user may conclude that photolysis is a possible or significant depletion mechanism for the chemical. However, further analysis to quantitatively estimate this depletion would require laboratory studies not possible within an emergency response time frame.

Volatilization may provide a significant attenuation mechanism for chemical spills on land. The rate of loss of chemicals from soil or surface pools due to volatilization is affected by many factors, such as the nature of the spill, soil properties, chemical properties, and environmental conditions. The mechanisms for chemical loss from the land are direct evaporation from a pool or saturated soil surface, vapor and liquid phase diffusion from chemicals incorporated into dry soil, and advection with vapor and liquid water due to capillary action (i.e. the wick effect). Thus, a comprehensive model of the volatilization process would be extremely complex; however, a number of relatively simple methods exist to estimate these losses, and three of them are presented here. (Thibodeaux, 1979; Hamaker, 1972; Swann et at, 1979). The reader is referred to the original literature or the text Handbook of Chemical Property Estimation Methods (Lyman et al, 1982) where a number of models are described along with conditions of use and parameter estimation methods.

Volatilization - Method 1

This method (Thibodeaux, 1979) is primarily applicable for a liquid pool of pure chemical. However, it can be used for a mixture of chemicals to estimate the reduction in the source concentration of one specific chemical due to the volatilization flux, assuming a constant volume mixture. It requires estimation of the area of the pool, wind speed at the spill site, pool temperature, and the Schmidt Number (Sc) for the chemical vapor.

The flux of chemical is given by:

$$N = 0.468 \ U^{.78} \ L^{-.11} \ Sc^{-.67} \ P_{vp} \ M/T \qquad (4.2)$$

where N = flux of chemical from pool, $\mu g/m^2/hr$

U = wind speed at 10m height, m/hr

$$L = \text{length of pool, m}$$

$$Sc = \text{Schmidt Number for chemical vapor (see below)}$$

$$P_{vp} = \text{chemical vapor pressure, mmHg}$$

$$T = \text{pool temperature, }^{O}K$$

$$M = \text{chemical molecular weight, g/mole}$$

The Schmidt number for a gas is defined by:

$$Sc = v/D \qquad (4.3)$$

where v = kinematic viscosity, cm^2/s

D = gas diffusion coefficient, cm/s

Schmidt numbers for many chemicals are tabulated by Thibodeaux (1979) and .nay be estimated for similar chemicals by the following equation:

$$\frac{S_{c1}}{S_{c2}} = \left(\frac{M_2}{M_1}\right)^{\frac{1}{2}} \qquad (4.4)$$

where M = molecular weight

Method 2

This method is applicable to situations in which the chemical has been applied to or spilled on the soil surface. Researchers at Dow Chemical Company (Swann et at, 1979) correlated volatilization rate with a number of chemical properties. The first-order rate constant for volatilization of chemicals spilled or applied to the soil was found to be approximated by the following correlation equation:

$$k_v = 4.4 \times 10^7 \frac{P_{vp}}{K_{oc}S} \qquad (4.5)$$

where k_v = volatilization rate constant. day^{-1}

K_{oc} = soil adsorption coefficient based on organic carbon content, ml/g

$$P_{vp} = \text{vapor pressure of chemical, mmHg}$$

$$S = \text{water solubility of chemical, } \mu g/ml$$

Since k_v is a first-order rate constant, the concentration loss function due to volatilization is represented as:

$$C = C_o \exp(-k_v t) \qquad (4.6)$$

where Co = initial concentration of the chemical, $\mu g/l$

C = concentration of the chemical after time t, $\mu g/l$

t = time, day

Method 3

This method (Hamaker, 1972) allows estimation of volatilization rates from chemicals distributed in a soil column such as after initial infiltration of a spill. It assumes a semi-infinite impregnated soil layer and no upward water flux. The loss of chemical is given by

$$Q_t = 2Co \ (Dt/\pi)^{\frac{1}{2}}$$

where

Q_t = total loss of chemical per unit area over time t, $\mu g/cm^2$

Co = initial concentration of chemical in the soil, $\mu g/cm^3$

D = diffusion coefficient of chemical vapor in the soil-air, cm^2/sec

t = time, sec

π = 3.14159...

For the situation where chemical is incorporated in moist soil, the upward flux of water due to evaporation and capillary action will greatly enhance the movement of chemical to the surface and its subsequent volatilization. Estimation of this flux requires use of a more complex model (e.g. Hamaker, 1972) which necessitates the determination of water fluxes in the soil. The user should recognize that Method 3 will significantly under-estimate volatilization under moist soil conditions.

Generally, the preceding methods require knowledge of vapor pressure, solubility and diffusion coefficients, all of which are available from sources previously identified (See Table 2.2). Additional sources of data for these methods, including the Schmidt number (Method 1), can be found in the following:

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1. Chemical Engineers Handbook (Perry and Chilton, eds., 1973)

2. Chemodynamics, (Thibodeaux, 1979)

3. Gaseous Diffusion Coefficients (Marrero and Mason, 1972)

4. Handbook of Chemical Property Estimation Methods (Lyman et al, 1982)

4.1.3 Nature of Soils and Geological Strata

A reliable study of contaminant movement through the unsaturated and/or saturated zones requires a careful assessment of the types of soils and/or geological formations present. The methodologies incorporated in this manual accept only homogeneous descriptions of the transport media being modeled, but users can choose parameter values that can partially account for any heterogeneities that are known to be present. For this reason, a thorough knowledge of the soils and geology at the site is important in the sound application of the relatively simple methods in this manual.

Data on the types of soils, presence of cracks or sinkholes, and occurrences of lenses of heterogeneous materials in the unsaturated zone can be found in soil surveys (performed by the U.S. Soil Conservation Service), well drillers' logs (usually kept by well owners or local departments of health or water), and construction design reports (on file with local engineering department or building inspector). If a soils expert is on the spill site, a quick evaluation of the general character of the surface material may be possible. The first aim of the soils assessment is the establishment of the predominant nature of the unsaturated zone so that the bulk density, porosity, organic content, and volumetric water content can be estimated. The presence of heterogeneities (cracks, clay lenses, sinkholes, etc.) can be used as a basis for adjusting the parameter values chosen under the assumption of homogeneity, or for interpreting the final model results.

An evaluation of the nature of the ground-water formations present at the site should include searches for prior hydrogeological investigations (by the U.S. Geological Survey, State Geological Survey and Department of Water Resources, and local and regional health and water agencies). A second major source of geological data lies with experts in universities, consulting firms, and government agencies. Drillers' well logs represent a third significant record of the composition of the saturated zone. Among the data being sought are the type of aquifers present (confined or water table), the predominant composition of the strata, the presence of fractures, and the existence of clay lenses. The assessment nomograph incorporated in this methodology is designed to simulate a single water table (unconfined) aquifer, but users should be aware of the existence of other types of aquifers and/or multiple water-bearing formations to assess the reliability of the predicted results and to perform qualitative assessments beyond the focus of the nomograph. Fractures can greatly increase the spread of contamination, while clay lenses retard this movement. Knowledge of their presence will govern the choice of parameter values and the interpretation of the predictions.

4.1.4 Age of the Waste Site or Spill

The age of the waste site or spill is essential in estimating the time duration of leaching of the contaminant into the unsaturated and saturated zones. For many surface spills, the investigation will occur immediately after the accident and the age of the site is therefore known. The analysis of newly-discovered uncontrolled disposal sites with the methodologies contained in this manual will require knowledge of the age of the site. Predictions of contaminant transport can then be related to real time and the extent of the plume at the time of the analysis can be estimated. To establish the age of an uncontrolled waste site, records of waste shipments should first be consulted. Any information found in the site records can be supplemented by tracing ownership of the property to determine the length of time the area was used as a landfill.

4.1.5 Depth to Ground Water

In evaluating transport in the unsaturated zone, the depth to ground water must be estimated in order to assess the likelihood that contaminants will reach the ground water. Since ground-water levels are often within 10 to 20 meters of the land surface, and can be 3 meters or less, the potential for ground-water contamination from waste sites and chemical spills is a significant problem. Seasonal fluctuations, if significant, should also be considered since these fluctuations can range from 1 to 5 meters or more in many parts of the country. Also, the effects of pumping and recharge areas should be evaluated.

Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.

Prior hydrogeologic and water supply studies in the general region of the site are valuable sources of data on site characteristics, including depth to ground water. Contact should be made with the U.S. Geological Survey, the State Geological Survey, the State Department of Water Resources, and the local and county water, health, and engineering departments as a start in the search for existing technical reports and information.

The depth to ground water can be determined by talking to the owners of nearby wells or by making depth measurements at these wells as long as the wells are not being actively pumped, and therefore accurately represent the water-table level. Also, water-surface elevations in nearby perennial streams, lakes, marshes, and other waterbodies (e.g., mines, gravel pits, flooded excavations) can be used to estimate the depth to ground water since these are areas where the ground-water surface intersects the land surface.

If prior studies, observations, or information from nearby wells are not available or do not provide the required data on depth to ground water, then local experts in hydrogeology (at universities, consulting firms, and governments agencies) should be contacted for guidance.

4.2   UNSATURATED ZONE PARAMETER ESTIMATION

Table 4.1 lists the nomograph parameters for an unsaturated zone assessment and the various types of information needed and/or useful for their evaluation. Except for contaminant concentration, which was discussed in Section 4.2, estimation guidelines for each parameter are provided below in the order shown in Table 4.1.

4.2.1 Pore Water Velocity

Estimation of pore water velocity is a necessary and important element in analyzing transport of contaminants through the unsaturated soil zone. In essence, the water (or other fluid) moving through the pore spaces in the soil is the driving mechanism for contaminant movement through the soil and to ground water. Although the term conventionally implies water movement, pore velocity could also refer to the movement of other solvents or fluids as might occur in a large volume chemical spill infiltrating through the soil.

Pore water velocity is a function of the volumetric flux per unit surface area and the volumetric water content, as follows:

$$V = \frac{q}{\theta} \tag{4.8}$$

Where V = pore water velocity, cm/day

q = volumetric flux per unit area, cm/day

θ = volumetric water content, dimensionless

In reality, the velocity of water movement through the unsaturated zone is a highly dynamic process resulting from the combined effects of stochastic rainfall inputs and soils, topographic, and vegetation characteristics of the site. However, under the steady flow assumption of our transport equation, the pore water velocity is assumed constant for the time period of interest. The specific time interval of concern also determines the appropriate method of estimating the volumetric flux, q, for the two types of problems addressed in this manual:

> Case 1 - Waste Sites: To assess the extent of the contaminant plume emanating from a leaking waste site, long-term or annual values of water infiltrating or percolating through the unsaturated zone of the site represents the volumetric flux, q. For the saturated zone, this value is also called the recharge rate representing the moisture actually reaching ground water.

> Case 2 - Spills: To estimate contaminant movement from a spill site, the volumetric flux is based on the volume of the spill (for large spills) and/or expected percolation/recharge volumes derived from short-term (5-day, 10-day, monthly) precipitation forecasts.

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TABLE 4.1 UNSATURATED ZONE PARAMETERS AND ASSOCIATED INFORMATION
NEEDED/USEFUL FOR EVALUATION

Parameter	Name	Information Needed/Useful For Evaluation
Co	Initial contaminant concentration	Contaminant identity, solubility, waste/site records, organic carbon partition coefficient, decay rates and processes
V	Pore water velocity	Meteorologic and soil characteristics, infiltration, percolation, volumetric water content, spill volume/waste quantity, soil porosity
k	Degradation/decay rate	Contaminant identity, relevant attenuation processes, environmental conditions
R	Retardation factor	Contaminant identity, adsorption characteristics, soil organic carbon, bulk density, ion exchange capacity, clay content/type, volumetric water content
D	Dispersion Coefficient	Subsurface/soil characteristics, pore water velocity, dispersivity

Guidelines and recommendations for estimating the volumetric flux for each case and the volumetric water content are presented below:

Percolation/Recharge

To estimate percolation and recharge values for a specific site, the conventional water balance equation can be written in the following form.

$$PER = P - ET - DR \tag{4.9}$$

where
PER = Percolation and Recharge, cm/yr
P = Precipitation, cm/yr
ET = Evapotranspiration, cm/yr
DR = Direct Surface Runoff, cm/yr

As a simplification for use within the emergency response time frame, the equation ignores any man-made water additions (e.g. irrigation, which could be added to P if known) and any change in soil moisture storage. PER includes both percolation and recharge to the ground-water systems of concern. For sites where the ground-water table is close to the land surface, percolation and recharge will be equal. However, for most sites where ground water is considerably below the surface, some of the percolating water will move laterally within the soil or upon reaching the ground-water surface, and subsequently discharge to a surface stream. Thus, PER should be used to assess contaminant movement through the unsaturated zone, but this value may need to be reduced to estimate recharge to deep aquifers or where impermeable strata exist.

A variety of local meteorologic and hydrologic data sources should be contacted to estimate percolation and recharge values for the specific site based on the water balance components of Equation 4.9. As discussed above, the appropriate time frame for the needed data and associated data sources will be different for Case 1 and Case 2 analyses.

Case 1 Analyses will require an estimate of the age of the waste site, or the time when hazardous waste releases may have begun, in order to determine the time period for the needed data. In most cases, this time period will be a number of years. In order of preference, the following methods of obtaining site-specific estimates of percolation and recharge are recommended:

1) Obtain annual estimates of PER from local sources and calculate an average value for the time period

2) Obtain annual estimates of P, ET, and DR from local sources, calculate annual values of PER from Equation 4.9 and calculate an average value for the time period.

3) Obtain mean annual values for PER from local sources, or obtain mean annual values of P, ET, and DR from which a mean annual value of PER can be calculated.

Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.

Local sources of historical data needed for estimating PER for Case 1 analyses include:

o   Local or regional water agencies

o   Local or regional offices of State and Federal water agencies (e.g. U.S. Geological Survey, National Weather Service; Forest Service, Department of Agriculture, EPA)

o   University libraries and departments of engineering, agriculture, soils, etc.

o   First order weather stations - usually found at airports

Lacking any local data, the user can obtain a preliminary estimate of mean annual percolation for areas in the eastern half of the U.S. from Figures 4.1 and 4.2, based on the U.S. Soil Conservation Service hydrologic soil classifications defined in Table 4.2. The isopleths of mean annual percolation in these figures were derived from application of the U.S. Soil Conservation Service Curve Number procedure (U.S. SCS, 1964) for estimating potential direct runoff at more than fifty sites in the Eastern U.S. (Stewart et al, 1976).

The Western U.S. was not included due to irrigation applications and the highly variable rainfall patterns and steep gradients (due to orographic effects) which preclude interpolation of percolation estimates between widely separated meteorologic stations.

To use these figures, the user must determine or estimate the hydrologic soil group for the soil at the waste site and then choose the appropriate figure for that class i.e.

A or B: Figure 4.1

C or D: Figure 4.2

Hydrologic soil groups for a variety of soils have been determined by the U.S. SCS (U.S. SCS, 1971); local offices and/or the state conservationist should be contacted for this information for the site. Alternately, Figure 4.3 provides an approximate mapping of hydrologic soil groups based on generalized soils information. Due to the extreme spatial variability of soil characteristics, Figure 4.3 should be used only as a last resort when site-specific information is not available.

Figure 4.4 provides an overview of the spatial variability of the three independent variables of the water balance equation - precipitation, evapotranspiration, surface runoff - on a national scale. This information is provided to supply the user with general background with which to assess possible major errors in locally supplied information. The national maps should not be used to estimate PER for a number of reasons; significant
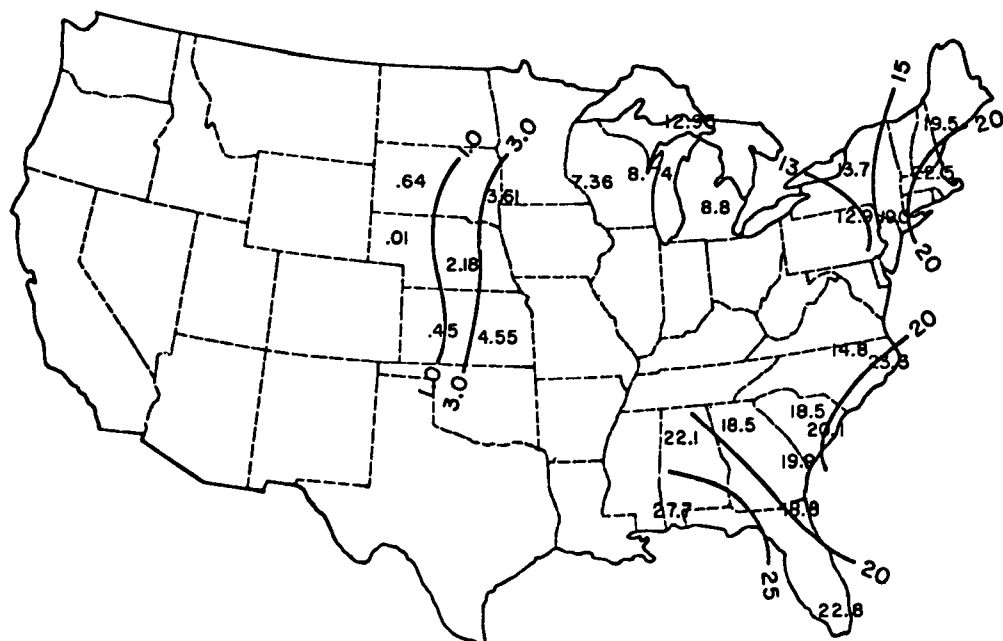
Figure 4.1a   Mean annual percolation below a 4-foot root zone in inches. Hydrologic Soil Group A. Four inches available water-holding capacity. Straight-row corn. (Stewart et al., 1976)
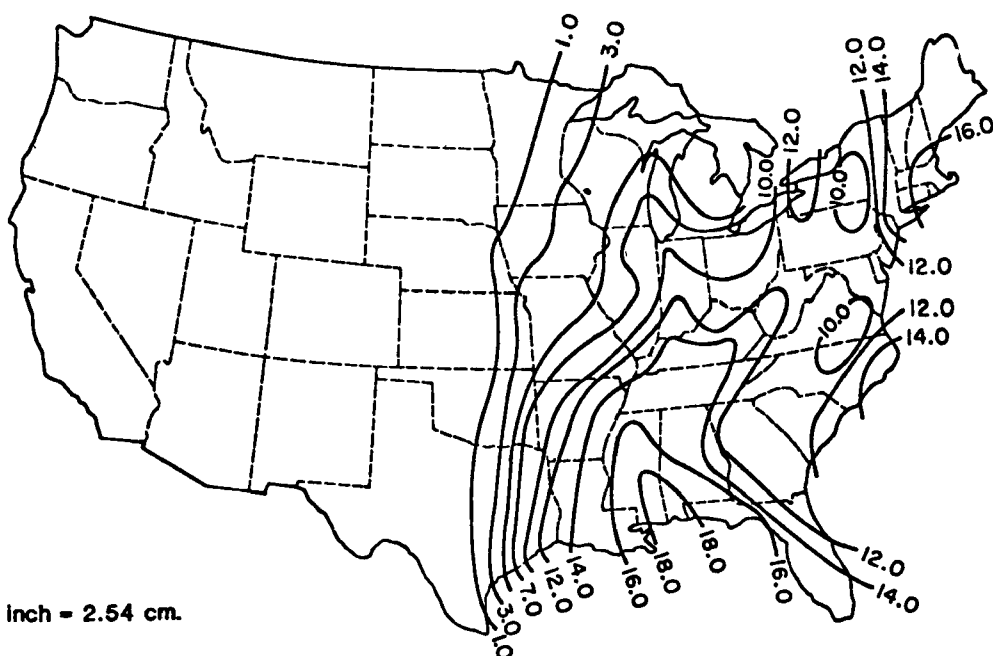
1 inch = 2.54 cm.

Figure 4.1b   Mean annual percolation below a 4-foot root zone in inches. Hydrologic Soil Group B. Eight inches available water-holding capacity. Straight-row corn. (Stewart et al., 1976)

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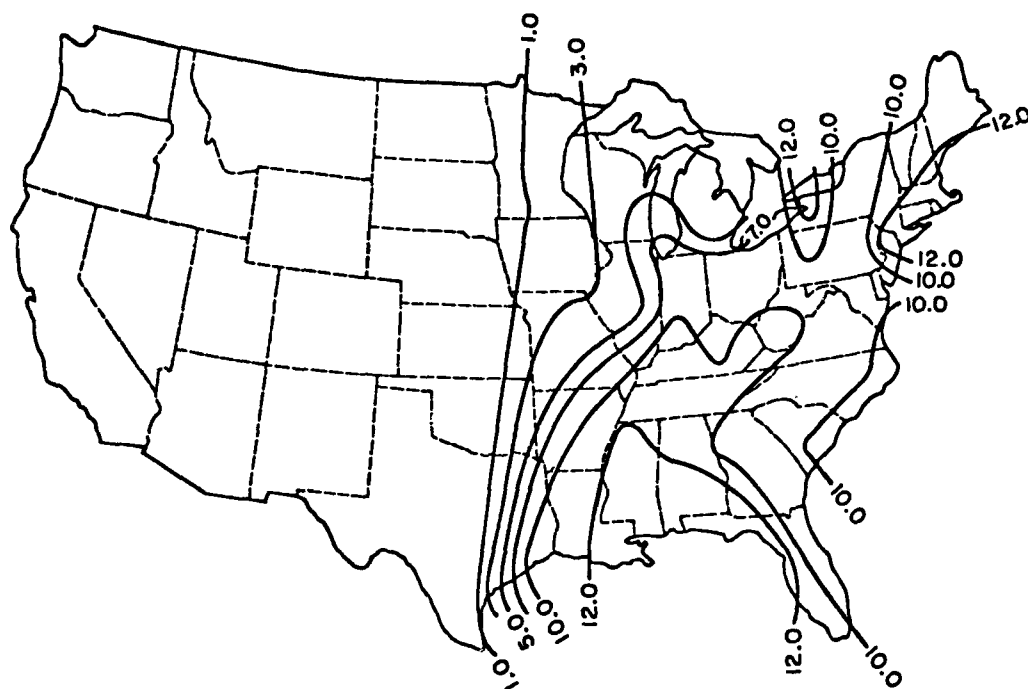
Figure 4.2a   Mean annual percolation below a 4-foot root zone in inches. Hydrologic Soil
Group C.   Eight inches available water-holding capacity. Straight-row corn.
(Stewart et al., 1976)

1 inch = 2.54 cm.
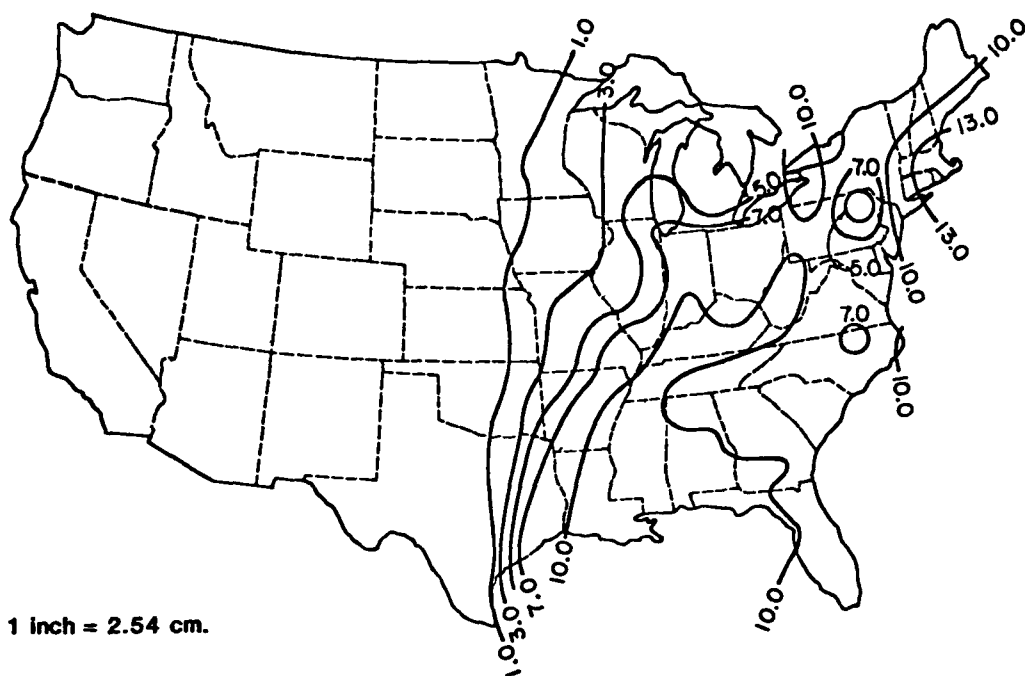
Figure 4.2b   Mean annual percolation below a 4-foot root zone in inches. Hydrologic Soil
Group D.   Six inches available water-holding capacity. Straight-row corn.
(Stewart et al., 1976)

TABLE 4.2 HYDROLOGIC SOIL CLASSIFICATIONS (U.S. SCS, 1964)

Group/Runoff Potential	Description
Group A. Low Runoff Potential	Soils having high infiltration rates even when thoroughly wetted and consisting chiefly of deep, well-to excessively-drained sands or gravels. These soils have a high rate of water transmission.
Group B. Moderately Low Runoff Potential	Soils having moderate infiltration rates when thoroughly wetted and consisting chiefly of moderately deep to deep, moderately well to well-drained soils with moderately fine to moderately coarse textures. These soils have a moderate rate of water transmission.
Group C. Moderately High Runoff Potential	Soils having slow infiltration rates when thoroughly wetted and consisting chiefly of soils with a layer that impedes downward movement of water, or soils with moderately fine to fine texture. These soils have a slow rate of water transmission.
Group D. High Runoff Potential	Soils having very slow infiltration rates when thoroughly wetted and consisting chiefly of clay soils with a high swelling potential, soils with a permanent high water table, soils with a claypan or clay layer at or near the surface, and shallow soils over nearly impervious material. These soils have a very slow rate of water transmission.

Figure 4.3   Generalized Hydrologic Soil Groups For The U.S. (Battelle, 1982)
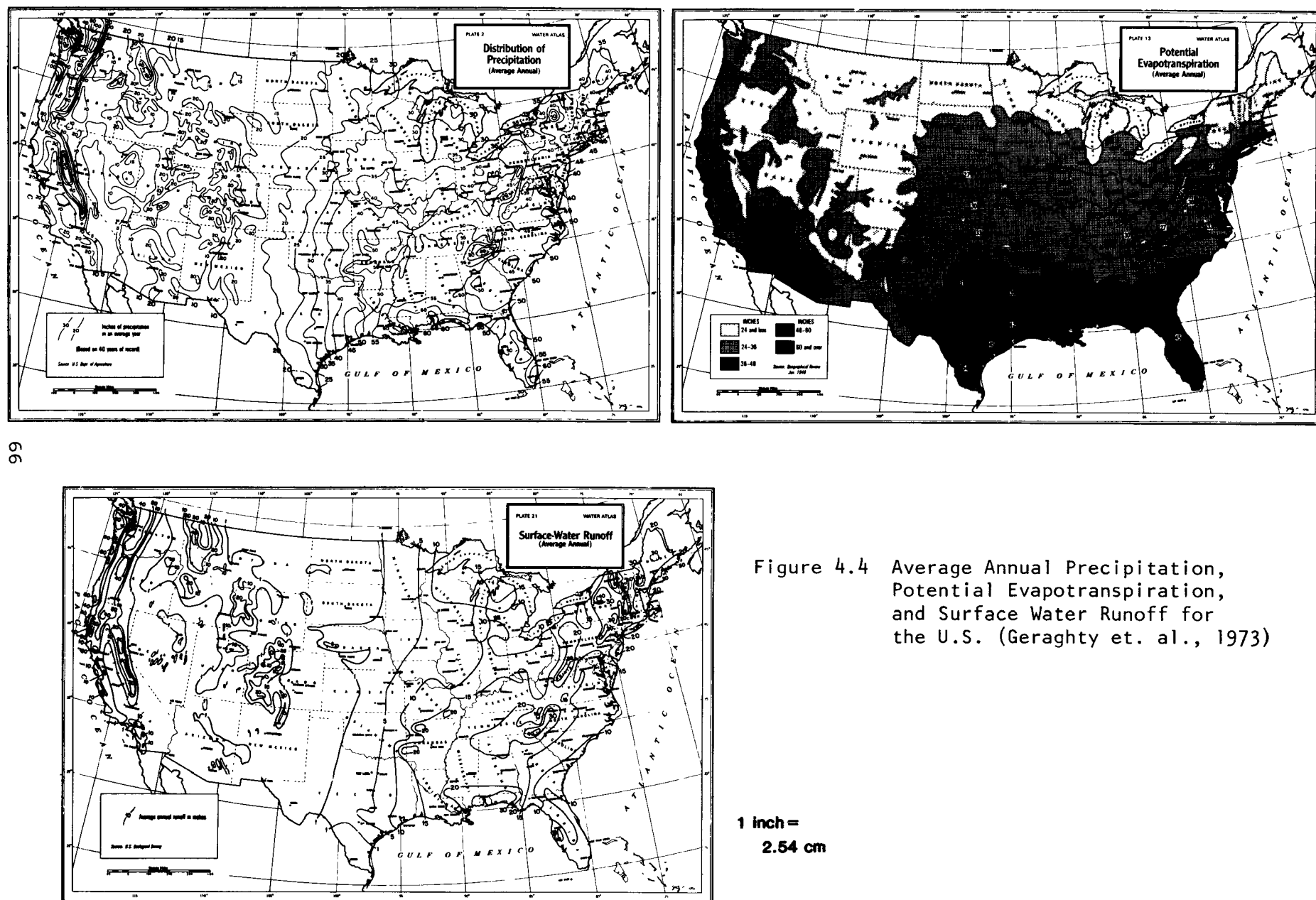
Figure 4.4 Average Annual Precipitation, Potential Evapotranspiration, and Surface Water Runoff for the U.S. (Geraghty et. al., 1973)

1 inch = 2.54 cm

local and regional variations are masked by the national isopleths; actual evapotranspiration is usually less than the potential evapotranspiration, especially in the arid west; surface runoff isopleths are derived from U.S.G.S. gaging station data which includes significant contributions of baseflow derived from ground water. In many areas of the country and especially the Western U.S., ignoring the runoff component in the calculation of annual PER values will not lead to significant errors, and may actually result in better percolation values since most runoff data include significant ground-water contributions.

Case 2 Analyses will require forecasts of expected future conditions, primarily rainfall and associated runoff, in order to assess the potential for ground-water contamination from a spill. The same water balance equation (Equation 4.9) is used to estimate PER but the P, ET, and DR terms must be evaluated differently from the Case 1 analyses. The primary differences result from the much shorter time frame of concern; spill situations will require assessment of the contaminant plume from a few days to a few months in the future in order to determine the appropriate emergency response actions. Because of this shorter time frame, recommendations for evaluating the water balance components are as follows:

1. P should be estimated from the quantitative precipitation forecasts (QPF) for the local region available from the local or regional office of the National Weather Service. Generally 5-day to 30-day forecasts are available; longer forecasts may often be qualitative in terms of "above-normal" or "below-normal" expected rainfall.

2. ET can be effectively ignored for the short time frames of 5 to 10 days without significant inaccuracy, especially during heavy rainfall periods. For time periods of one month or longer, ET estimates should be included in the water balance calculation.

3. Soil moisture storage and resulting effects on direct surface runoff become significant during the short time frame of a Case 2 analysis. Also, contaminated runoff although removed from the immediate spill site can reinfiltrate further downslope.

The same sources of local data noted under the Case 1 analysis are also important for a Case 2 analysis. One critical addition is the local or regional National Weather Service office; local precipitation forecasts are absolutely essential for a Case 2 analysis (except possibly in large-volume spills, discussed below). Other local information sources include TV/radio stations, local meteorologists, and other agencies either making or needing weather forecasts. Experience with local conditions in water agencies, universities, hydrologists, and other water experts is especially important in estimating ET and DR values for the short time frame analysis.

Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.

Lacking any local data, the user should consult the following publications which contain meteorologic data on a national scale:

1. **Climatic Atlas of the U.S.** (Environmental Data Service, 1968)

2. **Water Atlas of the U.S.** (Geraghty et al, 1973)

Both publications include various types of evaporation and evapotranspiration data. The Climatic Atlas also includes normal monthly precipitation on a national basis from which forecasts of above or below normal rainfall might be estimated. In addition, Thomas and Whiting (1977) have published annual and seasonal precipitation probabilities for 93 weather stations across the U.S. which could be used to further quantify qualitative forecasts.

Short term estimates of direct runoff from forecasted storm events are difficult to make, and are highly dependent on local site-specific conditions and existing soil moisture conditions. Lacking any local information or guidance from local hydrologists or water agencies, the user can choose runoff coefficients from Table 4.3 to estimate the portion of the rainfall that will result in runoff. The values in this table were derived by applying the SCS curve number procedure (U.S. SCS, 1964) for one-inch and four-inch storm events for each hydrologic soil group, and under each of the three antecedent soil conditions. Thus, the user should choose the low values in Table 4.3 for a one-inch forecast, the high value for a four-inch forecast, and prorate other forecasted amounts between the extremes. The values were developed for pasture land in good condition with an average slope of 2-5 percent; for more accuracy and/or significantly different land conditions the user should apply the SCS procedures directly as described in Appendix A.

The methodology in this manual is not directly applicable for large volume chemical spills where gravitational forces and the hydraulic pressure head (due to ponding) are the driving forces behind the chemical movement through the unsaturated zone. The primary reason for this is because the equations and parameters from which the nomograph was developed are based on **water** movement through porous media.

TABLE 4.3 RUNOFF COEFFICIENTS FOR HYDROLOGIC SOIL GROUPS*

5-Day Antecedent Rainfall
(inches)

Dormant Season 10/1-3/31	Growing Season 4/1-9/30	Hydrologic Soil Groups			
		A	B	C	D
<0.5	<1.4	0.0	0.0 -0.2	0.0 -0.14	0.0 -2.3
0.5-1.1	1.4-2.1	0.0-0.04	0.0 -0.20	0.02-0.40	0.08-0.51
>1.1	>2.1	0.0-0.18	0.07-0.49	0.22-0.66	0.36-0.75

*Derived from 1" to 4" rainfall events on pasture land kept in good condition with average slopes of 2-5 percent.

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However, if a qualitative or semi-quantitative assessment is required in an emergency situation, the methodology could be used for a gross or relative evaluation. The pore water velocity could be estimated by using the volume of the spill (i.e. area x average depth) and its infiltration rate to calculate the volumetric flux term in Equation 4.8; the infiltration rate might be grossly estimated by timing the drop in the surface of the ponded chemical, or estimating the total time for the ponded chemical to infiltrate or disappear. This estimated pore velocity could then be used, along with the other parameters (adjusted accordingly) in the methodology to estimate the concentration and time to enter the ground water. Clearly, the results will need to be analyzed and used with extreme caution, and only as a gross approximation. Chemicals with viscosities greater than water can be expected to move slower, while chemicals with a lower viscosity would likely move faster than water. The methodology predictions should be analyzed and adjusted in this manner.

For longer time frames, such as a few months, where infiltration from rainfall would be significantly greater than the spill volume, the pore water velocity should be derived from the water balance equation as described under the Case 2 analyses above.

Volumetric Water Content

The volumetric water content is the percent of the total soil volume which is filled with water. Under saturated conditions, the volumetric water content equals the total porosity of soil and is considerably less than porosity under unsaturated conditions. Conceptually, under steady flow conditions water (i.e. volumetric flux or percolation) is flowing through the pore spaces occupied by the volumetric water content. Thus, the flux and moisture content are directly related with higher flux values requiring higher moisture content, and vice versa.

Volumetric water content values will range from 5% to 10% at the low end to less than the total porosity (discussed below) at the higher end. For most soils, this results in a range of 5% to 50%. If no other local information is available, we recommend that the user select a value within this range (with the upper value modified to reflect total porosity of the site-specific soils) corresponding to the relative value of the flux as estimated by the percolation rate. Thus, for high percolation values (see Figures 4.1 and 4.2) water content values of 30% to 50% should be used, and for low percolation values 10% to 20% would be recommended. Alternately, the user may assume that the volumetric water content is equal to the field capacity for the particular soil type. Field capacity is the moisture retained by the soil after free drainage. Although this is not a rigorous definition, it is usually equal to the 1/3 bar soil moisture value by volume. Representative value ranges of field capacity by soil type are as follows:

	Field Capacity
Sandy soils	0.05 - 0.15
Silt/loam soils	0.13 - 0.30
Clay soils	0.26 - 0.45

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Total and Effective Porosity

The total porosity, usually stated as a fraction or percent, is that portion of the total volume of the material that is made up of voids. Effective porosity is less than total porosity, being reduced by the amount of space occupied by dead-end pores. In unconfined aquifers, the term specific yield, a measure of the quantity of water that will drain from a unit volume of aquifer under the influence of gravity, can be used as an estimate of effective porosity. The terms total and effective porosity are applicable to both the saturated and unsaturated zones.

Total porosity is required in the saturated and unsaturated zone methodologies in determining the retardation effects of adsorption. The effective porosity of the aquifer is necessary for calculating the velocity of flow within the voids using Darcy's Law. Effective porosity is not needed for the unsaturated zone analysis contained within this manual. Tables 4.4 and 4.5 provide representative values of total porosity and specific yield (an estimate of effective porosity) for several different soils and geologic materials.

4.2.2 Degradation Rate

The unsaturated zone can serve as an effective medium for reducing contaminant concentration through a variety of chemical and biological decay mechanisms which transform or attenuate the contaminant. Depending on chemical and soil characteristics, processes such as volatilization, biodegradation, hydrolysis, oxidation, and radioactive decay may be important in reducing concentrations prior to reaching the ground-water table. Also, both volatilization and photolysis may be important in reducing the concentrations of surface spills (see Section 4.1.2) and thus reduce the amount and concentration of contaminants available to move through the unsaturated zone.

The equations and nomograph for contaminant migration allow the use of a degradation or decay rate to represent disappearance of the pollutant by the attenuation mechanisms listed above. A first-order rate process is assumed with the degradation rate representing the aggregate disappearance rate of the compound by all significant decay or transformation processes. The input degradation rate is in units of inverse time (i.e. per day) and is related to the half-life of a compound as follows:

$$k = \frac{0.693}{t_{1/2}} \tag{4.10}$$

where k = degradation rate, day^{-1}
       $t_{1/2}$ = half-life, days

In evaluating an appropriate degradation rate, the following steps are recommended:

1. Determine if degradation can be significant for the specific time frame, compound, and situation being analyzed. For most instances

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TABLE 4.4 REPRESENTATIVE VALUES OF POROSITY

Material	Porosity, Percent	Material	Porosity, Percent
Gravel, coarse	28[a]	Loess	49
Gravel, medium	32[a]	Peat	92
Gravel, fine	34[a]	Schist	38
Sand, coarse	39	Siltstone	35
Sand, medium	39	Claystone	43
Sand, fine	43	Shale	6
Silt	46	Till, predominantly silt	34
Clay	42	Till, predominantly sand	31
Sandstone, fine-grained	33	Tuff	41
Sandstone, medium-grained	37	Basalt	17
Limestone	30	Gabbro, weathered	43
Dolomite	26	Granite, weathered	45
Dune Sand	45	Granite, weathered	45

[a] These values are for repacked samples; all others are undisturbed.

Source: Pettyjohn, W.A., et al, 1982

TABLE 4.5 SPECIFIC YIELDS, IN PERCENT, OF VARIOUS MATERIALS
(Rounded to nearest whole percent)

Material	# of Determinations	Specific Yield Max.	Min.	Ave.
Clay	15	5	0	2
Silt	16	19	3	8
Sandy clay	12	12	3	7
Fine sand	17	28	10	21
Medium sand	17	32	15	26
Coarse sand	17	35	20	27
Gravelly sand	15	35	20	25
Fine gravel	17	35	21	25
Medium gravel	14	26	13	23
Coarse gravel	14	26	12	22

Source: Pettyjohn, W.A. et al, 1982

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involving the fate and movement of non-persistent compounds, degradation should be considered. However, high concentrations of toxic chemicals may effectively sterilize the soil and reduce or eliminate microorganisms that biologically degrade the compound.

Also, if decay of the compound is extremely slow relative to the time frame of interest, or if daughter products produced by transformation are also toxic, the user may decide to ignore degradation in order to estimate maximum potential concentrations.

2. Assess the major decay mechanisms for the specific compound of concern.

3. Evaluate compound-specific rates for each major decay mechanism.

4. Use the sum of the decay rate or the maximum if one decay mechanism is predominant, as the value of the decay rate for the assessment nomograph calculations.

The same information sources used in identifying the compound may be helpful in determining major decay or loss mechanisms and associated rate values. Companies associated with the waste/spill incident, or companies within the same industry, can be an extremely valuable source of this information.

Table 4.6 provides a summary of the relative importance of different chemical fate processes for a wide variety of compounds in various classifications. If the specific compound is not included in Table 4.6, industry sources may be able to provide the classification or names of other compounds with similar degradation mechanisms. (For example, volatilization is a major process for most halogenated aliphatic hydrocarbons). Although Table 4.6 was developed primarily for the aquatic environment, it may be appropriate for many spill situations and appears to be the best summary of the relative importance of different chemical processes for a variety of compounds. The user should confirm the validity of the compound-specific information in Table 4.6 with any other available data.

Degradation rates for specific mechanisms have been compiled for numerous chemicals and hazardous compounds in the following publications:

1. Physical/Chemical Properties of Hazardous Waste Constituents, Dawson et al (1980).

2. Aquatic Fate Process Data for Organic Priority Pollutants, Mabey et al (1982) (Note: This publication includes available data for all compounds listed in Table 4.6, except metals and inorganics).

3. Handbook of Environmental Data on Organic Chemicals, Verschueren, K. (1977).

Also, degradation rates for pesticides in both field and laboratory conditions have been collected and published by Rao and Davidson (1980), Nash (1980), and Wauchope and Leonard (1980). This information is based on

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TABLE 4.6 RELATIVE IMPORTANCE OF PROCESSES INFLUENCING AQUATIC FATE OF PRIORITY POLLUTANTS (After Mills et al., 1982; Callahan et al., 1979)

Compound	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
PESTICIDES						
Acrolein	-	+	+	+	-	-
Aldrin	+	+	?	-	-	+
Chlordane	+	+	?	-	-	+
DDD	+	+	-	-	-	+
DDE	+	+	-	+	-	+
DDT	+	+	-	-	+	+
Dieldrin	+	+	-	+	-	+
Endosulfan and Endosulfan Sulfate	+	+	+	?	+	-
Endrin and Endrin Aldehyde	?	?	?	+	-	+
Heptachlor	+	+	-	?	++	+
Heptachlor Epoxide	+	-	?	?	-	+
Hexachlorocyclohexane (α,β,δ isomers)	+	?	+	-	-	-
-Hexachlorocyclohexane (Lindane)	+	-	+	-	-	-
Isophorone	-	-	?	+	-	-
TCDD	+	-	-	?	-	+
Toxaphene	+	+	+	-	-	+
PCBs and RELATED COMPOUNDS						
Polychlorinated Biphenyls	+	+	+[a]	?	-	+
2-Chloronaphthalene	-	?	+	+	-	-
HALOGENATED ALIPHATIC HYDROCARBONS						
Chloromethane (methyl chloride)	-	+	-	-	-	-
Dichloroethane (methylene chloride)	-	+	?	-	-	-
Trichloromethane (chloroform)	-	+	?	-	-	-
Tetrachloromethane (carbon tetrachloride)	?	+	-	-	-	?
Chloroethane (ethyl chloride)	-	+	?	-	+	-
1,1-Dichloroethane (ethylidene chloride)	-	+	?	-	-	-
1,2-Dichloroethane (ethylene dichloride)	-	+	?	-	-	-
1,1,1-Trichloroethane (methyl chloroform)	-	+	-	-	-	-
1,1,2-Trichloroethane	?	+	-	-	-	?
1,1,2,2-Tetrachloroethane	?	+	-	-	-	?

Key to Symbols:

++ Predominant fate determining process
+ Could be an important fate process

- Not likely to be an important process
? Importance of process uncertain or not known

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TABLE 4.6 continued

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Hexachloroethane	?	?	?	?	?	+
Chloroethene (vinyl chloride)	+	-	-	-	-	-
1,1-Dichloroethene (vinylidene chloride)	?	+	?	-	-	?
1,2-trans-Dichloroethene	-	+	?	-	-	-
Trichloroethene	-	+	?	-	-	-
Tetrachloroethene (perchloroethylene)	-	+	+	-	-	-
1,2-Dichloropropane	?	+	-	?	+	?
1,3-Dichloropropene	?	+	-	?	+	-
Hexachlorobutadiene	+	+	?	-	?	+
Hexachlorocyclopentadiene	+	+	-	+	+	+
Bromomethane (methyl bromide)	-	+	-	-	+	-
Bromodichloromethane	?	?	?	?	-	+
Dibromochloromethane	?	+	?	?	-	+
Tribromomethane (bromoform)	?	+	?	?	-	+
Dichlorodifluoromethane	?	+	-	?	-	?
Trichlorofluoromethane	?	+	-	-	-	?
HALOGENATED ETHERS						
Bis(choromethyl) ether	-	-	?	-	++	-
Bis(2-chloroethyl) ether	-	+	-	-	-	?
Bis(2-chloroisopropyl) ether	-	+	-	-	-	?
2-Chloroethyl vinyl ether	-	+	?	-	+	-
4-Chlorophenyl phenyl ether	+	?	?	+	-	+
4-Bromophenyl phenyl ether	+	?	?	+	-	+
Bis(2-chloroethoxy) methane	-	-	?	-	+	?
MONOCYCLIC AROMATICS						
Benzene	+	+	-	-	-	-
Chlorobenzene	+	+	-	?	-	+
1,2-Dichlorobenzene (o-dichlorobenzene)	+	+	-	?	-	+
1,3-Dichlorobenzene (m-dichlorobenzene)	+	+	?	?	?	+
1,4-Dichlorobenzene (p-dichlorobenzene)	+	+	-	?	-	+
1,2,4-Trichlorobenzene	+	+	-	?	-	+
Hexachlorobenzene	+	-	-	-	-	-

Key to Symbols:
++ Predominant fate determining process   - Not likely to be an important process
+ Could be an important fate process   ? Importance of process uncertain or not known

TABLE 4.6 continued

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Ethylbenzene	?	+	?	-	-	-
Nitrobenzene	+	-	-	+	-	-
Toluene	+	+	?	-	-	-
2,4-Dinitrotoluene	+	-	-	+	-	?
2,6-Dinitrotoluene	+	-	-	+	?	?
Phenol	-	+	+	+	-	-
2-Chlorophenol	-	-	?	+	-	-
2,4-Dichlorophenol	-	-	++	-	-	-
2,4,6-Trichlorophenol	?	-	?	?	-	-
Pentachlorophenol	+	-	+	+[b]	-	+
2-Nitrophenol	-	-	-	++[b]	-	-
4-Nitrophenol	+	-	-	++[b]	-	-
2,4-Dinitrophenol	+	-	-	++[b]	-	-
2,4-Dimethyl phenol (2,4-xylenol)	-	-	?	+	-	-
p-chloro-m-cresol	-	-	?	++	-	-
4,6-Dinitro-o-cresol	+	-	-	++	?	?

PHTHALATE ESTERS

Compound	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Dimethyl phthalate	+	-	+	-	-	+
Diethyl phthalate	+	-	+	-	-	+
Di-n-butyl phthalate	+	-	+	-	-	+
Di-n-octyl phthalate	+	-	+	-	-	+
Bis(2-ethylhexyl) phthalate	+	-	+	-	-	+
Butyl benzyl phthalate	+	-	+	-	-	+

POLYCYCLIC AROMATIC HYDROCARBONS

Compound	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Acenaphthene[c]	+	-	+	+	-	-
Acenaphthylene[c]	+	-	+	+	-	-
Fluorene[c]	+	-	+	+	-	-
Naphthalene	+	-	+	+	-	-
Anthracene	+	+	+	+	-	-
Fluoranthene[c]	+	+	+	+	-	-
Phenanthrene[c]	+	+	+	+	-	-
Benzo(a)anthracene	+	+	+	+	-	-
Benzo(b)fluoranthene[c]	+	-	+	+	-	-
Benzo(k)fluoranthene[c]	+	-	+	+	-	-
Chrysene[c]	+	-	+	+	-	-

Key to Symbols:
++ Predominant fate determining process
+ Could be an important fate process
- Not likely to be an important process
? Importance of process uncertain or not known

TABLE 4.6 continued

Compound — Process

Compound	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Pyrene[c]	+	-	+	+	-	-
Benzo(ghi)perylene[c]	+	-	+	+	-	-
Benzo(a)pyrene	+	+	+	+	-	-
Dibenzo(a,h)anthracene[c]	+	-	+	+	-	-
Indeno(1,2,3-cd)pyrene	+	-	+	+	-	-
NITROSAMINES AND MISC. COMPOUNDS						
Dimethylnitrosamine	-	-	-	++	-	-
Diphenylnitrosamine	+	-	?	+	-	?
Di-n-porpyl nitrosamine	-	-	-	++	-	-
Benzidine	+	-	?	+	-	-
3,3'-Dichlorobenzidine	++	-	-	+	-	-
1,2-Diphenylhydrazine (Hydrazobenzene)	+	-	?	+	-	+
Acrilonitrile	-	+	?	-	-	+
METALS AND INORGANICS						
Asbestos	+	-	-	-	-	-
Antimony	+	-	-	-	+	+
Arsenic	+	+	+	-	+	+
Berylumm	+	-	?	-	+	-
Cadmium	+	-	-	-	+	+
Copper	+	-	-	-	+	+
Chromium	+	-	-	-	+	+
Cyanides	-	+	+	+	-	-
Lead	+	-	+	+	-	+
Mercury	+	+	+	+	-	+
Nickel	+	-	-	-	+	-
Selenium	+	+	+	-	+	+
Silver	+	-	-	-	-	-
Thallium	+	-	-	-	-	+
Zinc	+	-	-	-	+	+

Key to Symbols:

++ Predominate fate determining process
+ Could be an important fate process

- Not likely to be an important process
? Importance of process uncertain or not known

Notes

[a] Biodegradation is the only process knoen to transform polychlorinated biphenyls under environmental conditions, and only the lighter compounds are measurably biodegraded. There is experimental evidence that the heavier polychlorinated biphenyls (five chlorine atoms or more per molecule) can be photolyzed by ultraviolet light, but there are no data to indicate that this process is operative in the environment.

[b] Based on information for 4-nitrophenol

[c] Based on information for PAH's as a group. Little or no information for these compounds exists.

agricultural pesticide applications and should be used with caution for the waste/spill situation only if other data is lacking.

4.2.3 Retardation Factor

The process of adsorption of contaminants onto soil particles and associated organic matter retards the movement of the contaminant through both unsaturated and saturated media. As discussed in Section 3, the adsorption process is included in the assessment nomograph by the retardation factor which is defined as follows:

$$R = 1 + \frac{B}{N} K_d \qquad (4.11)$$

where R = Retardation factor (dimensionless)

B = Bulk density, g/cc

N = Effective porosity (saturated conditions), or θ, volumetric water content (unsaturated conditions), dimensionless

K_d = Partition coefficient, ml/g

Thus, the major determinant of the retardation factor, R, is the partition coefficient, K_d, which represents the ratio of the adsorbed pollutant concentration to the dissolved (or solution) concentration. Under the linear, equilibrium isotherm assumption employed in this manual, the form and units of K_d are as follows:

$$K_d = \frac{Cs}{Cw} \qquad (4.12)$$

Where K_d = Partition coefficient (ml/g)

C_s = Pollutant concentration on soil (ppm)

C_w = Pollutant concentration in water (mg/l)

Since B and N usually vary within a small range of values and K_d can vary by many orders of magnitude, the resulting value of R is primarily determined by K_d, which in turn is a function of the specific compound and soil combination.

Guidelines for estimating N, either as total porosity under saturated conditions or volumetric water content under unsaturated conditions, are presented in Section 4.2.1. Guidelines for evaluating K_d and B are discussed below.

Partition Coefficient

Since K_d can have a different value for each compound and soil combination, values of K_d from previous studies (or other sources) at the

waste/spill site should be used whenever possible. For most spill sites and many waste sites, this information will not be available and K_d will need to be estimated by other means.

For neutral organic compounds, a body of knowledge has been developed over the past decade (see Lyman et al, 1982) whereby K_d values can be estimated from the soil organic carbon content and the organic carbon partition coefficient for the compound as follows:

$$K_d = K_{oc} \frac{OC}{100} \qquad (4.13)$$

where K_{oc} = Organic carbon partition coefficient (ml/g)

OC = Percent organic carbon content of soil or sediment (dimensionless)

Equation 4.13 assumes that the organic carbon in the soil or sediment is the primary means of adsorbing organic compounds onto soils and sediments. This concept has served to reduce much of the variation in K_d values for different soil types.

K_{oc} values for a number of chemicals and hazardous compounds have been tabulated by Rao and Davidson (1980), Dawson et al (1980) and Mabey et al (1982). Also, a variety of regression equations relating K_{oc} to solubility, octanol-water partition coefficients (K_{ow}), and other compound characteristics have been developed; Table 4.7 from Lyman et al (1982) presents the major regression equations available, the chemical classes represented, the number of compounds investigated, and the associated correlation coefficient. Users should review the discussion by Lyman et al (1982) to comprehend the limitations, assumptions, and parameter ranges underlying the equations in Table 4.7. K_{oc} estimates from more than one equation should be evaluated in order to assess the variability in the estimates.

Data on the compound characteristics needed for the regression equations can be obtained from Dawson et at (1980), Mabey et al (1982), and other sources listed in Table 2.2. Also, a very complete data base of K_{ow} values is maintained by Dr. Corlan Hansch at Pomona College, Pomona, California (714-621-8000 ext. 2225). This data base is available in microfiche form for easy use in the field. K_{oc} values should be used directly whenever available; otherwise estimation of K_{oc} from K_{ow} is appropriate.

Organic Carbon/Organic Matter Content

Organic content of soils is described in terms of either the percent organic carbon, which is required in our estimation of K_d, or the percent organic matter. These two values are conventionally related as %OC = %OM/1.724.

Typical values of percent organic matter range from 0.4% to 10.0% (Brady, 1974). Table 4.8 lists the range and average organic matter content for mineral surface soils in various parts of the U.S; organic soils, such as

Regression Equations for the Estimation of K_{oc}

Eq. No.	Equation[a]	No.[b]	r^2[c]	Chemical Classes Represented	Ref.
4-5	$\log K_{oc} = -0.55 \log S + 3.64$ (S in mg/L)	106	0.71	Wide variety, mostly pesticides	[26]
4-6	$\log K_{oc} = -0.54 \log S + 0.44$ (S in mole fraction)	10	0.94	Mostly aromatic or polynuclear aromatics; two chlorinated	[25]
4-7[d]	$\log K_{oc} = -0.557 \log S + 4.277$ (S in μ moles/L)	15	0.99	Chlorinated hydrocarbons	[11]
4-8	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	45	0.74	Wide variety, mostly pesticides	[26]
4-9	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	19	0.95	Aromatics, polynuclear aromatics, triazines and dinitroaniline herbicides	[9]
4-10	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10	1.00	Mostly aromatic or polynuclear aromatics; two chlorinated	[25]
4-11	$\log K_{oc} = 0.94 \log K_{ow} + 0.02$	9	e	s-Triazines and dinitroaniline herbicides	[7]
4-12	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	13	0.91	Variety of insecticides, herbicides and fungicides	[36]
4-13[d]	$\log K_{oc} = 0.524 \log K_{ow} + 0.855$	30	0.84	Substituted phenylureas and alkyl-N-phenylcarbamates	[6]
4-14[d,f]	$\log K_{oc} = 0.0067 (P - 45N) + 0.237$	29	0.69	Aromatic compounds: ureas, 1,3,5-triazines, carbamates, and uracils	[18]
4-15	$\log K_{oc} = 0.681 \log BCF(f) + 1.963$	13	0.76	Wide variety, mostly pesticides	[26]
4-16	$\log K_{oc} = 0.681 \log BCF(t) + 1.886$	22	0.83	Wide variety, mostly pesticides	[26]

a. K_{oc} = soil (or sediment) adsorption coefficient; S = water solubility; K_{ow} = octanol-water partition coefficient; BCF(f) = bioconcentration factor from flowing-water tests; BCF(t) = bioconcentration factor from model ecosystems; P = parachor; N = number of sites in molecule which can participate in the formation of a hydrogen bond.

b. No. = number of chemicals used to obtain regression equation.

c. r^2 = correlation coefficient for regression equation.

d. Equation originally given in terms of K_{om}. The relationship $K_{om} = K_{oc}/1.724$ was used to rewrite the equation in terms of K_{oc}.

e. Not available.

f. Specific chemicals used to obtain regression equation not specified.

TABLE 4.7   REGRESSION EQUATIONS FOR THE ESTIMATION OF K_{oc}.   Lyman et al., 1982. (Reference numbers keyed to Lyman et al., 1982, Chapter 4)

peat or muck soils, can have values in the range of 15% to 20% or greater. Agricultural soils are commonly in the range of 1% to 5% organic matter. Figure 4.5 shows a national distribution of % Nitrogen in the surface foot of soil; % Nitrogen and %OC are generally related as %OC = 11 x % N. This information can be used to estimate %OM and %OC as a basis for determining K_d.

The values in Table 4.8, and those mentioned above are primarily for the top 15cm of the soil profile. Organic content normally decreases sharply with depth, as shown in Figure 4.6 which compares the relative change in percent organic matter with depth for a prairie soil and a forest soil. Below 60 cm in depth, percent organic matter values of less than 2% are common. Users must evaluate appropriate %OM values for the specific region or regions of the soil profile through which the contaminant will be moving. Thus for surface spills, a weighted value of surface and subsurface %OM for the unsaturated zone should be used; whereas subsurface releases from waste sites will require the subsurface %OM at the appropriate depth. For many subsurface or saturated zone releases, a %OM value of less than 1% may be reasonable.

Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.

TABLE 4.8   AVERAGE ORGANIC MATTER CONTENTS AND RANGES OF
MINERAL SURFACE SOILS IN SEVERAL AREAS OF THE
UNITED STATES
(Lyon et al, 1952)

Soils	Organic Matter (%)	
	Range	Av.
240 West Va. soils	0.74-15.1	2.88
15 Pa. soils	1.70- 9.9	3.60
117 Kansas soils	0.11-3.62	3.38
30 Nebraska soils	2.43-5.29	3.83
9 Minn. prairie soils	3.45-7.41	5.15
21 Southern Great Plains soils	1.16-2.16	1.55
21 Utah soils	1.54-4.93	2.69

Retardation Factors for Ionic Species

The processes which govern the adsorption of substances which ionize are very different from those for substances that are nonionic. Most soils have

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NITROGEN

Percent N

Highly Diverse
Insufficient Data

Under 0.05

0.05 - 0.09

0.10 - 0.19

0.20 and Over
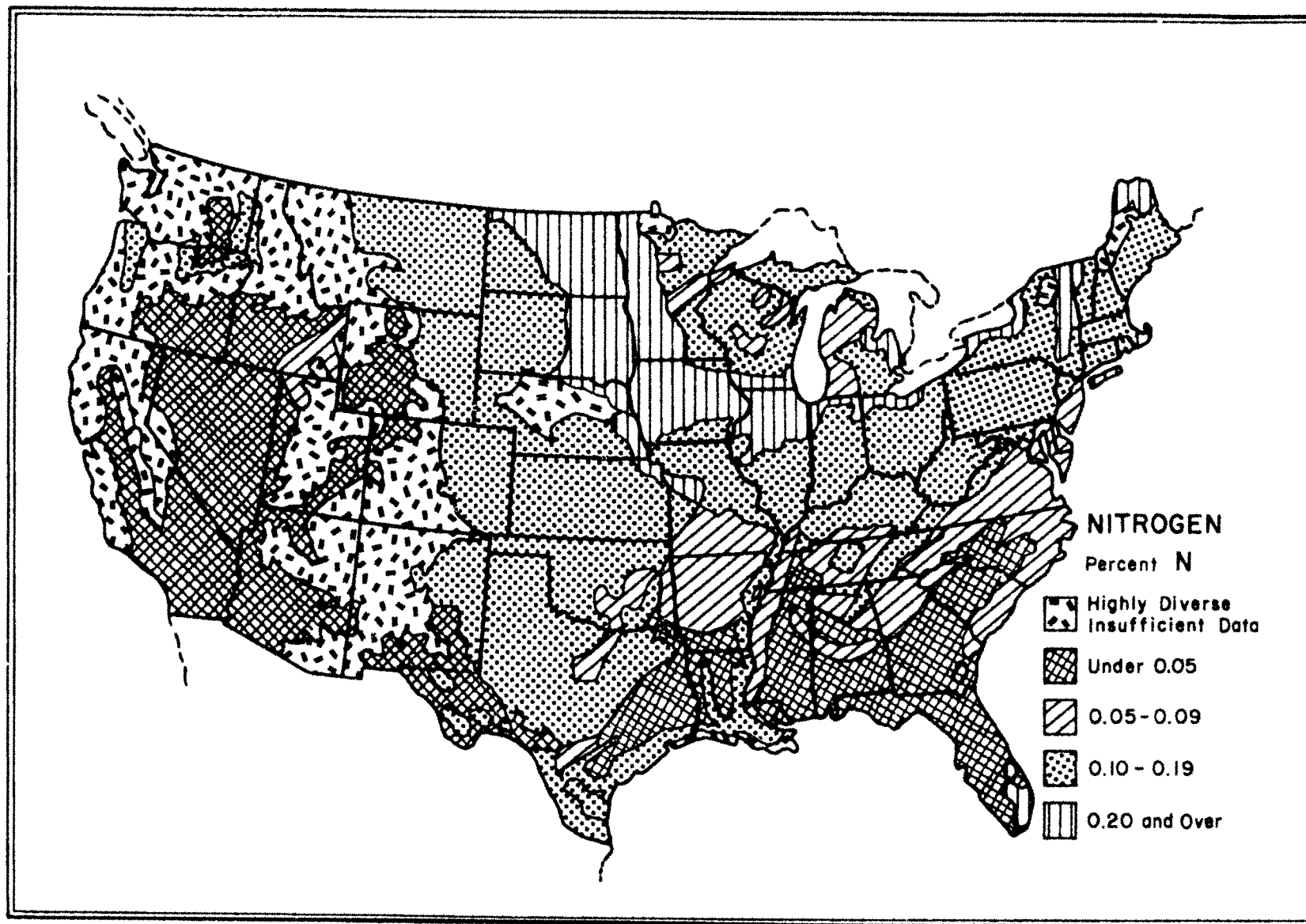
Figure 4.5   Percentage Nitrogen (N) In Surface Foot Of Soil (Parker, et al., 1946)

PRAIRIE SOIL (Minn.)   FOREST SOILS (Indiana)

Well drained   Poorly drained   Well drained   Poorly drained

PERCENT ORGANIC MATTER IN SOIL
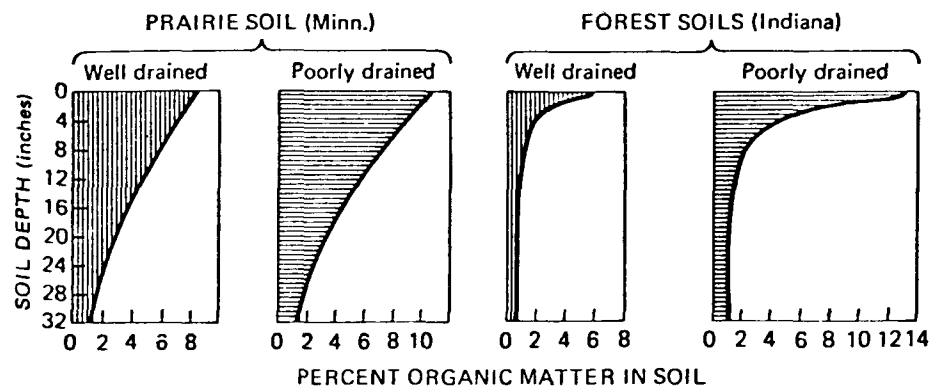
Figure 4.6 - Distribution of organic matter in four soil
             profiles. (Brady, 1974)

a net negative charge, and therefore ions that are positively charged are attracted to them. Some positively charged ions are preferentially adsorbed to soil materials and will displace other positively charged ions already on the exchange sites. This process is referred to as cation exchange or base exchange. Anions (negatively charged particles) can either be attracted or repelled by soil particles depending upon the net charge of the soil. The anion exchange capacity of soils is usually less than cation exchange capacity, unless extremely low pH's are encountered or high amounts of Fe or Al oxides, or hydroxides are present. A rule of thumb is that anion repulsion (negative adsorption) is roughly 1 to 5% of the cation exchange capacity (CEC) in non-alkaline soils, and up to 15% in alkaline soils (pH 8.5) (Bolt, 1976).

Acids and Bases in Solution - By definition acids are substances which give-up (donate) protons (hydrogen atoms) in solution. Bases, on the other hand, take-on (accept) protons from solution. A typical reaction for a monoprotic (one hydrogen) acid dissolved in water is

$$HA \quad = \quad H^+ \quad + \quad A^- \tag{4.14}$$

where the double arrow indicates an equilibrium dissociation reaction. The ratio between the products and reactants in this reaction is always a constant known as the dissociation constant, K_a, where

$$K_a = \frac{[H^+] \ [A^-]}{[HA]} \tag{4.15}$$

K_a is usually expressed as a logarithm, pK_a,

$$pKa = -\log (K_a) \tag{4.16}$$

The reaction for a monoprotic base in solution is

$$B + H_2O \quad = \quad HB^+ \quad + \quad OH^- \tag{4.17}$$

and the reaction constant is

$$K_b = \frac{[HB^+] \ [OH^-]}{[B]} = \frac{[HB^+] \ Kw}{[B] \ [H^+]} \tag{4.18}$$

The constants pK_a, pK_b, and pK_w are related by

$$14 = pK_a + pK_b = pK_w \qquad (4.19)$$

for any given compound. K_w is the dissociation constant for water, equal to 10^{-14}.

Retardation Factor for Acids and Bases - If the constants pK_a or pK_b are known for an acid or base and the pH of the solution is known, the fraction of unionized acid, or base can be determined. For the acid the fraction unionized acid is

$$\alpha = \left(\frac{1 + K_a}{[H^+]} \right)^{-1} \qquad (4.20)$$

For a base, the fraction unionized is

$$\beta = \left(\frac{1 + K_b[H^+]}{K_w} \right)^{-1} \qquad (4.21)$$

If we assume that the ionized portion of the acid is unattracted to soil materials, then the retardation factor for the acid is

$$R_{acid} = 1 + \alpha \frac{K_d B}{n} \qquad (4.22)$$

For the base we will assume that the ionized portion is exchanged similarly to any monovalent ion ($Kd \approx 100$) and that the unionized portion is adsorbed hydrophobically. Thus, the retardation factor for the base is

$$R_{base} = \frac{1 + \beta K_d B + 100 (1 - \beta)}{n} \qquad (4.23)$$

The value of K_d in either of these cases is determined exactly as described above for the neutral (nonionic) species.

The number 100 in Equation 4.23 is an estimate of $K_d^+ B/n$ for a model monovalent cation. This number can range from less than 1 up to 10^5 for

various species. A substitute for this number for a particular soil can be estimated by

$$B \frac{K_d^+}{n} = \frac{CEC}{100 \sum z^+} \frac{B}{n} \qquad (4.24)$$

when Kd^+ = adsorption partition coefficient for the charged cation, cc/g

CEC = cation exchange capacity of the soil, milliequivalents/100g

$\sum z^+$ = sum of all positively charged species in the soil location, milliequivalents/cc

The quantity $\sum z^+$ is about 0.001 for most agricultural soils.

In reality, the exchange of the cation or anion is governed by a selectivity coefficient which varies for different soils, and competing ion pairs. When the ionized substance is adsorbed, it reduces the concentration of ionized substances in solution which causes more of the unionized substance to accept or donate protons. Thus, for strongly adsorbed ions, the concentration of the substance in solution could approach very small values. On the other hand if the selectivity for the ion is low or repulsion occurs, virtually all the substance could remain in solution. Thus, the above approach will give an answer between these two extremes; a conservative assumption would be a retardation factor of 1.

To use this methodology, the user should first decide whether the substance is an organic acid or base. This may not be easy to determine. If the substance is not listed in the tables in this section or one does not have prior knowledge about the compound, a retardation factor of 1 should be used. Some pK_a and pK_b values for specific compounds are found in Tables 4.9 and 4.10. Values of $pK_a > 14$ indicate fully protonated forms, while values < 0 indicate fully deprotonated forms of the acid; for bases, pK_b values less than 0 indicate complete protonation while values greater than 14 indicate a completely deprotonated form.

Harris and Hayes (1982) give references which contain pK_a and pK_b values for various organic acids and bases. These are listed below:

Dissociation Constants of Organic Acids in Aqueous Solution, (Kortum et al 1961)

Dissociation Constants for Organic Bases in Aqueous Solution, (Perrin, 1965)

Ionization Constants of Organic Acids in Aqueous Solution (Sergeant and Dempsey, 1979)

TABLE 4.9 pK_a VALUES FOR SELECTED ORGANIC ACIDS

Compound	pKa	Ref.
Aliphatic Acids	3.8 - 5.0	A
Acetic Acid (Substituted)	0.2 - 4.3	A
Aliphatic Acids (Diabasic)		A
1st Carboxyl	1.3 - 4.3	
2nd Carboxyl	4.3 - 6.2	
p-Aminobenzoic Acid		B
K_1 (NH_3 group)	2.29	
K_2 (COOH group)	4.89	
m-Aminobenzoic Acid		B
K_1 (NH_3 group)	3.07	
K_2 (COOH group)	4.73	
m-Aminophenol		B
K_1 (NH_3 group)	4.17	
K_2 (OH group)	9.87	
Aminocyanomethane	5.34	B
Aniline	27.	B
Benzoic Acid	4.2	A
Benzoic Acid (Halogenated)		A
Ortho	2.8 - 3.3	
Meta	3.8	
Para	3.9 - 4.1	
3-Bromo-4-methoxy anilinium ion	4.08	B
Bromoacetic Acid	2.90	B
But-3-enoic Acid	4.34	B
t-Butane	19.	B
Benzoic Acid (Dicamba)	1.93	C
Benzoic Acid (Amiben)	3.40	C
p-Cyanophenol	7.95	B
4-Chloro-3-nitroanilinium ion	4.08	B
Cyanoacetic Acid	2.47	B
Chloromethylphosphonic Acid	1.40	B
Carboxylic Acids	4.5 ± 0.5	B
$CH_3OH_2^+$	-2	B
$C_6H_5OH_2^+$	-6.7	B
2-Chlorophenol	8.52	D
Dichloroacetic Acid	2.90	B
2, 4 Dichlorophenol	7.85	D
2, 4 Dinitrophenol	4.04	D
2, 4 Dimethylphenol	10.6	D
4, 6-Dinitro-o-cresol	4.35	D
Glycine		B
K_1	2.35	
K_2	9.78	
Hydroxymethylphosphonic Acid	1.91	B
p-Methoxybenzoic Acid	4.47	B

(Continued)

TABLE 4.9 (Cont.)

Compound	pKa	Ref.
m-Methylsulfonybenzoic Acid	3.52	B
Methane	40.	B
p-Nitrophenylarsenic Acid	2.90	B
p-Nitrophenol	7.2	B
p-Nitroanilinium	1.0	C
2-Nitrophenol	7.21	D
4-Nitrophenol	7.15	D
Phenol	10.	A, B
m-Phenoxybenzoic Acid	4.47	B
Pyridinium Ion	5.2	B
Phenoxy Acid (2, 4D)	2.8	C
Picolinic Acid (Picloram)	1.90	C
Phenol (Dinoseb)	4.4	C
Pentachlorophenol	4.74	D
RNH_3^+	10.	B
p-Tolyacetic Acid	4.37	B
Tetralol-2	10.48	B
1, 3, 5 - Trihydroxybenzene (K_1)	8.45	B
Trifluoroacetic Acid	0.23	B
Toluene	35	B
2,4, 6 Trichlorophenol	5.99	D

References:

    A.   Stevenson, 1982

    B.   Harris and Hayes, 1982

    C.   Weed and Weber, 1974

    D.   Mills et al, 1982

TABLE 4.10 pK_b VALUES FOR SELECTED ORGANIC BASES

Compound	pKa	Ref.
Aliphatic Amine Homologues	3.10-4.20	A
Anilines (substituted)	6.90-9.40	A
Acetanilide	13.6	A
Acetamide	14.5	A
Atrazine	12.32	C
Amitrole	9.83	C
Benzidine	9.34, 10.43	D
$CH_3:^-$	-26	B
$C_6H_5CH_2:^-$	-21	B
$C_6H_5NH:^-$	-13	B
$C_4H_9O:^-$	-5	B
$C_6H_5O:^-$	4.0	B
Carboxylate Anions	9.5 ± 0.5	B
Methanol	16	B
$p-NO_2-C_6H_4O:^-$	6.8	B
p-Nitroaniline	13.0	B
Pyridine	8.8	A,B
Pyrimidine	12.7	A
Phenol	20.7	B
Propazine	12.15	C
Prometryne	9.95	C
Prometone	9.72	C
RHN_2	4.00	B
Simazine	12.35	C

References:
A. Stevenson, 1982

B. Harris and Hayes, 1982

C. Weed and Weber, 1974

D. Mills et al, 1982

Bulk Density

Bulk density is the mass of a unit volume of dry soil, as measured in the field, usually expressed in g/cc or lb/ft³. The entire volume is taken into consideration including both solids and pore spaces. Thus, loose porous soils will have low values of bulk density and more compact soils will have higher values. Bulk density values normally range from 1.0 to 2.0 g/cc, and soils with high organic matter content will generally have low bulk density values.

Brady (1974) has presented the following ranges of bulk density for selected surface soil types commonly found in agricultural areas:

	Bulk Density (g/cc)
well-decomposed organic soil	0.2 - 0.3
cultivated surface mineral soils	1.25 - 1.45
clay, clay loam, silt loam	1.00 - 1.60
sands and sandy loams	1.20 - 1.80

Ritter and Paquette (1967) have listed the following bulk density ranges for material classes encountered in road and airfield construction:

	Bulk Density (g/cc)
silts and clays	1.3 - 2.0
sand and sandy soils	1.6 - 2.2
gravel and gravelly soils	1.8 - 2.3

Subsoils will generally be more compact than surface soils and thus have higher bulk densities. Very compact subsoils regardless of texture can have bulk densities of 2.0 g/cc or greater; values of 2.3 to 2.5 g/cc should be considered as upper limits. Because of this relatively small range of values, users can choose bulk density values for the waste/spill site from the above information if local site-specific data are not available. Mean or average values for a soil type can be used, and if no data are available a value of 1.5 g/cc can be used with reasonable accuracy for many soils.

4.2.4 Dispersion Coefficient

The dispersion process is exceedingly complex and difficult to quantify, especially for the unsaturated zone. It is sometimes ignored in the unsaturated zone, with the reasoning that pore water velocities are usually large enough so that pollutant transport by convection i.e. (water movement) is paramount. Consequently, unless site specific information or studies are available to establish that dispersion is or is not significant, and data is available to estimate the dispersion coefficient, we recommend that the user perform at least two separate assessments. The first assessment would ignore dispersion and the second assessment should include a reasonable value of a dispersion coefficient to evaluate the importance of dispersion in the unsaturated zone for the specific site. A dispersion coefficient, D, of 0.01 will effectively ignore dispersion and subsequently simplify

calculations. However, dispersion should not be ignored for saturated zone analyses. Since most available information on dispersion is for ground-water systems, discussion and parameter guidelines for the dispersion coefficient are provided in Section 4.3.3. Users should consult that section to estimate a coefficient for the unsaturated zone.

4.3 SATURATED ZONE PARAMETER ESTIMATION

Table 4.11 lists the parameters required for a saturated zone assessment and the types of information needed or useful in their estimation. The following sections provide guidelines for estimating each of these input parameters in the order shown in Table 4.11.

4.3.1 Effective Aquifer Thickness (or Zone of Mixing)

The extent of the aquifer subject to contamination is described using an effective aquifer thickness which represents a zone of mixing. For good mixing between the ground water and the contaminant, this effective thickness may equal the total thickness of the aquifer. However, in most cases it will be less than the total thickness, especially for deep aquifers. In cases where the pollutant has a significantly different density and/or viscosity than water, the extent of mixing may be reduced and the contaminant plume will be concentrated over only a portion of the aquifer's thickness. The saturated zone methodology in this manual assumes that the chemical pollutant mixes with the ground water to the effective thickness or mixing zone. The model does not consider immiscible wastes or portions of wastes that either entirely float on top of the water table or sink to the bottom of the aquifer and remain there. For example, the major portion of gasoline is immiscible in water and its total movement in the subsurface cannot be studied effectively with this manual. However, that portion of gasoline that is soluble in water can be analyzed using the assessment methodology.

Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.

The user should search for prior hydrogeological investigations in the offices of Federal, State, County, and Municipal agencies as the initial step in gathering estimates of the total thickness of the aquifer being studied. Hydrogeologists in neighboring universities, consulting firms, and government agencies are another possible source of data on the structural thickness of water-bearing strata and may be able to provide recommendations for an effective mixing depth. If these reports and contacts are not helpful, nearby well owners can be consulted. The perforated intervals of their water supply wells provide a lower limit estimate of the thickness of underlying aquifers since most wells are not perforated for the entire thickness. This information, contained on their drilling logs, should be used carefully and only in the absence of other data.

An estimate of the minimum thickness to use for the mixing zone can be obtained as follows:

Table 4.11   SATURATED ZONE PARAMETERS AND ASSOCIATED INFORMATION
NEEDED/USEFUL FOR EVALUATION

Parameter	Name	Information Needed/Useful for evaluation
m	Effective aquifer thickness (or zone of mixing)	Aquifer characteristics, total aquifer thickness, contaminant density, ground-water density
V	Ground-water (interstitial pore water) velocity	Hydraulic conductivity, hydraulic gradient, effective porosity, specific yield
D	Dispersion coefficient	Aquifer characteristics, dispersivity, molecular diffusion, ground-water velocity
R	Retardation factor	Partition coefficient, bulk density, total porosity, K_{oc}, ionic characteristics
k	Degradation/decay rate	Contaminant identity, relevant attenuation processes, environmental conditions
Co	Source contaminant concentration	Contaminant identity, solubility, waste/site records, organic carbon partition coefficient, decay rates and processes, unsaturated zone assessment.

$$m = \frac{q\ L}{V_d} \qquad\qquad (4.25)$$

where

m   =   effective (minimum) aquifer thickness, m

q   =   recharge from the site, cm/day

V_d =   Darcy flow velocity, cm/day

L   =   Width of leachate plume at water table, m

Equation 4.25 calculates the minimum aquifer thickness that will accept recharge from the site based on the aquifer properties; calculation of V_d is discussed in the next section. This calculated minimum value should be used only as a guide to the lower limit of a reasonable mixing zone depth.

In assessing which portion of the total aquifer thickness is subject to mixing with the contaminant, knowledge of the density and viscosity of the ground water and the pollutant is needed. Major differences in these characteristics indicate a tendency toward reduced mixing and therefore a smaller effective thickness.

In the temperature range normally expected in ground water, the water density can be assumed as 1 g/cc or 62.4 lb/ft^3. Viscosity is generally reported in units of centipoise (.01 g/sec-cm) and common values for organic liquids are in the range of 0.3 to 20 centipoise at ambient temperatures; water has a viscosity of 1 centerpoise at 20°C (Grain, 1982). To establish these characteristics of the contaminant, first measure or estimate its temperature, and then determine its density from one of the following sources:

1.   OHM-TADS - U.S. EPA Data Base.

2.   CHRIS Manuals - U.S. Coast Guard, 1974.

3.   Dangerous Properties of Industrial Materials by N.I. Sax, 1979.

4.   Handbook of Environmental Data on Organic Chemicals, by Verschueren, 1977.

5.   The Merck Index, Merck and Co., (Windholz, 1976)

6.   Physical/Chemical Properties of Hazardous Waste Constituents, U.S. EPA, 1980.

Information on viscosity is less wide-spread. Data can be found in the Handbook of Chemistry and Physics (Weast 1973) and in Grain (1982) which is contained in the Handbook of Chemical Property Estimation Methods (Lyman et al, 1982); Grain (1982) also provides methods of estimating viscosity from other chemical data.

Information on the compound may also be available from experts in the chemical industry or at universities.

The estimation of effective aquifer thickness will be quite difficult because of uncertainties concerning the mixing properties of the contaminant. It is recommended that a range of thickness values be used in the computation to evaluate the effect of errors in estimating this parameter on the predicted pollutant concentrations.

4.3.2 Ground-Water (Interstitial Pore Water) Velocity

The velocity of ground-water flow within the voids (i.e., interstitial pore water velocity) is required as an input to the saturated zone methodology in this manual. If the value of this parameter has not been established in previous investigations it can be calculated by using Darcy's Law.

In the Darcy equation, the Darcy flow velocity, V_d is equal to the product of the saturated hydraulic conductivity, K, and the hydraulic gradient, $\frac{dh}{dl}$ as follows:

$$V_d = -K \frac{dh}{dl} \tag{4.26}$$

To determine the flow velocity in the voids, the Darcy velocity is adjusted to account for the area actually available for flow:

$$V = \frac{K}{n_e} \frac{dh}{dl} \tag{4.27}$$

where n_e is the effective porosity.

Total and effective porosity are discussed in Section 4.2, while hydraulic conductivity and gradient are discussed below.

Hydraulic Conductivity

Saturated hydraulic conductivity is a measure of the quantity of liquid that can flow through a unit cross-sectional area of a medium with time, while under the influence of a hydraulic gradient. It is a function of the permeability of the medium as well as the density and viscosity of the flowing liquid. In ground-water systems, the fluid is water, existing within a fairly narrow range of temperatures, and hydraulic conductivity and permeability can therefore be directly related. Hydraulic conductivity is sometimes referred to as the coefficient of permeability, a term that should not be confused with permeability as discussed above.

In this manual, hydraulic conductivity is a required input for the saturated zone analysis if the ground-water velocity is unknown and must be determined using Darcy's Law as discussed above. The units of hydraulic conductivity are those of velocity (L/T) or alternatively, flow per unit area. In the ground-water (saturated zone) methodology used in this manual, flow and therefore hydraulic conductivity are considered only in the horizontal direction.

Tables 4.12 and 4.13 contain values of horizontal hydraulic conductivity (K) and permeability (k) for a variety of geologic media. As can be seen in these tables, hydraulic conductivity increases with increasing particle size and with increasing occurrences of fractures. These values should be used only if site specific information is not available.

Ground-Water Flow Gradient

In order to determine the velocity of ground-water flow using Darcy's Law, the ground-water flow hydraulic gradient must be estimated. The flow gradient is influenced by both natural and man-made factors. In most cases, ground water moves in roughly the same direction as surface water drainage, and the ground-water flow gradient varies in magnitude in a direct relationship with surface topography (i.e. the gradient is steepest where the land slopes most steeply and vice versa). Man-made influences on the flow gradient include artificial recharge areas (disposal wells), areas of enhanced recharge (landfills) and pumping wells. Areas of increased recharge tend to cause the ground water to flow radially outward from the recharge point, while pumping wells tend to cause ground water to flow radially inward towards the well. These artificial influences on the ground-water flow patterns may be **very important** in assessing the local **magnitude** and **direction** of the ground-water flow gradient.

Data on the ground-water flow gradient should be sought in existing hydrogeological reports from the U.S. Geological Survey, state water and geological agencies, and local health, water, and engineering departments. Experts in the engineering and geology departments of nearby universities, in consulting firms, and in government agencies may also be able to provide guidance. Also, water table elevations at several points in the area can be used to estimate the gradient and direction (See Section 4.1.5 for estimating depth to ground water).

Local site-specific information should be used whenever possible; significant errors can result from using general or regional data.

If these data sources are not helpful, the flow gradient can be roughly estimated as equivalent in magnitude and direction to the general slope of the land surface in the area of the waste/spill site. This estimate will suffer from substantial error if significant pumping or artificial recharge is occurring in the area. It is most appropriate as a regional estimate of ground-water flow, and becomes less valid when applied to smaller regions.

4.3.3 Dispersion Coefficient

Hydrodynamic dispersion in subsurface media is a process that causes the spreading of a contaminant beyond that which results from convection alone. Variations in local velocity (magnitude and direction) give rise to dispersive spreading on microscopic, macroscopic, and regional scales. The magnitude of dispersion varies significantly with the scale of the analysis,

RANGE OF VALUES OF HYDRAULIC CONDUCTIVITY AND PERMEABILITY
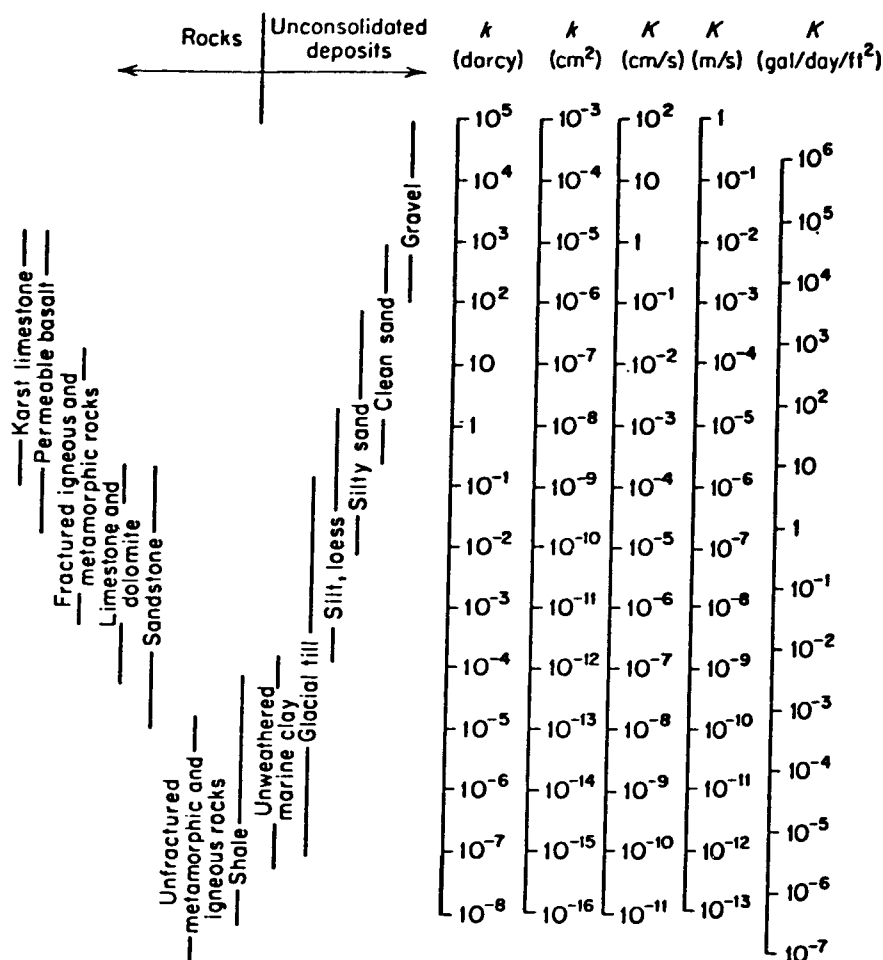
CONVERSION FACTORS FOR PERMEABILITY AND HYDRAULIC CONDUCTIVITY UNITS

	Permeability, k*			Hydraulic conductivity, K		
	cm^2	ft^2	darcy	m/s	ft/s	gal/day/ft²
cm^2	1	1.08×10^{-3}	1.01×10^8	9.80×10^2	3.22×10^3	1.85×10^9
ft^2	9.29×10^2	1	9.42×10^{10}	9.11×10^5	2.99×10^6	1.71×10^{12}
darcy	9.87×10^{-9}	1.06×10^{-11}	1	9.66×10^{-6}	3.17×10^{-5}	1.82×10^1
m/s	1.02×10^{-3}	1.10×10^{-6}	1.04×10^5	1	3.28	2.12×10^6
ft/s	3.11×10^{-4}	3.35×10^{-7}	3.15×10^4	3.05×10^{-1}	1	5.74×10^5
gal/day/ft²	5.42×10^{-10}	5.83×10^{-13}	5.49×10^{-2}	4.72×10^{-7}	1.74×10^{-6}	1

*To obtain k in ft², multiply k in cm² by 1.08×10^{-3}.

TABLE 4.12 RANGE OF VALUES OF HYDRAULIC CONDUCTIVITY AND PERMEABILITY. (After Freeze and Cherry, 1979)

TABLE 4.13 REPRESENTATIVE HORIZONTAL FIELD HYDRAULIC
CONDUCTIVITY RANGES FOR SELECTED ROCKS

Rock	Horizontal Field Hydraulic Conductivity (gpd/sq ft)	
Gravel	1×10^3	$- 3\times 10^4$
Basalt	1×10^{-6}	$- 2\times10^4$
Limestone	2×10^{-2}	$- 2\times10^4$
Sand and gravel	2×10^2	$- 5\times10^3$
Sand	1×10^2	$- 3\times10^3$
Sand, quick	50	$- 8\times10^3$
Dune sand	1×10^2	$- 3\times10^2$
Peat	4	$- 1\times10^2$
Sandstone	1×10^{-1}	$- 50$
Loeses	2×10^{-3}	$- 20$
Clay	2×10^{-4}	$- 2$
Till	5×10^{-4}	$- 1$
Shale	1×10^5	$- 1\times10^1$

Source: Pettyjohn et at (1982)

Note: 1 gpd/sq. ft. = 4.72 x 10^{-5} cm/sec

and choosing appropriate coefficients often requires careful assessment of earlier studies. Applications of this manual for rapid assessment of potential ground-water contamination may be directed toward either local or regional evaluation of contaminant plume migration. Consequently, prior investigations may not provide data on an appropriate scale for the application.

For both the unsaturated and saturated zones, the effects of dispersion are based upon the input of dispersion coefficients with dimensions of L^2/T. These coefficients incorporate two forms of the dispersive process, dynamic dispersion (or dispersivity) and molecular diffusion. For typical flow velocities, molecular diffusion is a negligible part of total dispersion (Pettyjohn et al 1982), and thus it is often ignored.

In a saturated zone assessment, a longitudinal (horizontal) and transverse dispersion coefficient is required as an input parameter. As discussed earlier, the dispersion coefficient, D, is made up of a molecular diffusion component and a dynamic dispersion component as follows:

$$D = aV + D^* \tag{4.28}$$

where D = Total dispersion coefficient, cm^2/day

a = Dispersivity, cm

V = Ground-water (interstitial) velocity, cm/day

D^* = Molecular diffusion coefficient, cm^2/day

Dispersivity is far more significant than molecular diffusion except when ground-water flow velocities are very low (Freeze and Cherry, 1979). Table 4.14 provides regional dispersivities determined in earlier studies in a variety of aquifer types; dispersivities for local or small scale applications may be less than these values by an order of magnitude or more.

Evidence indicates that a general rule of thumb for dispersivity would be to set it equal to 10% of the distance measurement of the analysis (Gelhar and Axness, 1981). Thus, for a well or stream 100 meters down gradient from the source, a dispersivity of 10 meters would be appropriate. For the unsaturated zone, a 5-meter depth to ground water would require a 0.5 m dispersivity. This approximate rule of thumb, along with Table 4.14 and discussion above, should help the user to estimate a dispersion coefficient in the absence of other data. Sensitivity analyses on the dispersion coefficient are strongly recommended.

4.3.4 Retardation Factor

In using a nomograph for evaluating landfill permits, Pettyjohn et al (1982) recommend that a retardation factor of 1.0 be used unless the permit applicant can show that retardation is significant through field data and testing. In effect, this produces a "worst case" situation since retardation is ignored and the contaminant is routed straight through the aquifer. Since ion exchange is the major retardation mechanism for the saturated zone (since organic matter content is usually low), the clay

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TABLE 4.14 REGIONAL DISPERSIVITIES (a)

Type of aquifer	Location	Longitudinal dispersivity (a_x) (ft)
Alluvial sediments	Rocky Mountain Arsenal, Co	100
	Colorado	100
	California	100
	Lyon, France	40
	Barstow, CA	200
	Sutter Basin, CA	260-6600
	Alsace, France	49
Glacial deposits	Long Island, N.Y.	70
	Alberta, Canada	10-20
Limestone	Brunswick, GA	200
Fractured basalt	Idaho	300
	Hanford site, Washington	100
Glacial till	Alberta, Canada	10-20
Limestone	Cutler area, Fla.	22
	Hypothetical	0.01-100 70 33 1.6-330

Source: Pettyjohn, et al, 1982

Note: 1 ft. = .3048 m

content of the aquifer material tends to control retardation. In performing a saturated zone assessment, if the user feels that retardation is significant based on contaminant characteristics and aquifer composition, the guidelines for estimating the retardation factor in Section 4.2.3 may assist in evaluation; otherwise a value of R = 1 is recommended.

4.3.5 Degradation/Decay Rate

Degradation and decay mechanisms are generally more significant in surface and unsaturated soils than in ground water. However, hydrolysis and chemical oxidation can occur in saturated media, and anaerobic decomposition is possible even in deep aquifers. Considering the long travel times that occur in most ground-water systems, even decay rates that correspond to half-lives of 2 years or more can substantially reduce ground-water concentrations prior to discharge to a well or surface waters. Consequently, the user should carefully consider the use of a non-zero decay rate in the saturated zone assessment and analyze the impacts of a reasonable range of decay rates for the compound of concern. Section 4.2.2 discusses estimation of decay rates and sources of information.

4.3.6 Source Contaminant Concentration

As described previously, the assessment nomograph requires source contaminant concentration in ground water as a critical input parameter for a saturated zone assessment. If contaminant movement through the unsaturated zone is important, the Co value for the saturated zone is based upon the concentration predicted by the unsaturated zone and the linkage procedures described in Section 3.3. If the water table is sufficiently high so that the leachate directly enters ground water, the Co value is the estimate of the leachate concentration (see Section 4.1.2).

SECTION 5

EXAMPLE APPLICATIONS AND RESULT INTERPRETATION

Two examples are given to demonstrate how the assessment nomograph and accompanying worksheets can be used for assessments of emergency response situations involving continuous input and pulse input of contaminants to the unsaturated zone with subsequent linkage to the saturated zone.

The nomographs and worksheets are computational tools for evaluation of contaminant concentrations at different values of x and t. As mentioned in Section 3, the user must determine from the potential hazards of the emergency situation which $C(x,t)$ values need to be evaluated. If a time response is desirable $C(x)$ should be evaluated at different values of t; or if a profile response is needed, $C(t)$ should be evaluated at different x values.

In most emergency response situations especially involving chemical or waste spills, time responses which provide expected contaminant concentrations and time of arrival at the ground-water table and/or at a point in the aquifer are usually needed. This is the type of information an On-Scene Coordinator may need, to assess the potential for ground-water contamination and associated emergency actions. Profile responses are not often evaluated in a rapid assessment situation, but they are helpful in showing the movement of a contaminant through the unsaturated or saturated zones.

For both examples below, time responses for both the unsaturated and saturated zones are calculated and plotted as they are commonly needed for emergency assessments. In the first example, a profile response is also evaluated in order to familiarize the user with the associated calculation steps and some fundamental concepts of fate and transport phenomena. Since time responses are most often needed for subsequent saturated zone assessments, the unsaturated zone results are further interpreted and analyzed to demonstrate how time responses are used as input to the subsequent saturated zone assessment.

5.1 EXAMPLE #1: ASSESSMENT OF A CONTINUOUS CONTAMINANT SOURCE

Consider a recently discovered (continuous) leak of an industrial solvent from a surface storage tank. The following data are developed from past investigations conducted by the company and chemical characteristics of the solvent:

V	= 0.55 cm/day	B	= 1.5 gm/cm^3
D	= 13.75 cm^2/day	θ	= 0.15

100

$$k = 0.004 \text{ day}^{-1} \qquad\qquad Co = 1500 \text{ mg/l}$$

$$K_d = 0.07 \text{ ml/gm}$$

Depth to water table = 250 cm

The worksheet in Table 5.1 describes the development of the above parameter values under the 'Data Sources/Comments' heading.

5.1.1 Evaluation of Profile Responses

Concentration profiles expected to result from this chemical leak are evaluated at different times to show the potential movement of the compound. As shown in Table 5.1, three profiles are evaluated at 50, 200, and 1000 days after the leak began. The calculations are performed according to the procedures discussed in Section 3.1.4. Results of these profile responses -- concentrations (C/Co) vs depth (x) at specific times (t) -- are plotted in Figure 5.1.

The plot (Figure 5.1) indicates that most of the compound remains in the top 20 cm of the soil for 50 days. In 200 days, the compound has leached below 150 cm, and in 1000 days, steady-state is attained. While moving downward, the chemical is being adsorbed and degraded. With a retardation factor of 1.7, very little retardation is occurring. Degradation is the major cause for the decrease in concentration values found at greater depths.

5.1.2 Evaluation of Time Response at the Ground-Water Table

The time response is evaluated at the ground-water table. In this example, the mean depth to ground water was 250 cm. Concentrations at different times are estimated as shown in the worksheet, Table 5.2, according to the procedures presented in Section 3.1.4. Results are plotted in Figure 5.2.

The plot (Figure 5.2) shows a steady state concentration of 300 mg/l (C/Co = 0.20) at the ground-water table. This concentration is then used to develop the source concentration (Co) for the saturated zone assessment.

5.1.3 Evaluation of Time Response in Ground Water

The spill site is located 100 m up gradient from a local stream that supplies a water supply reservoir. The goal of the assessment is to determine when and in what concentrations the contaminant plume will reach the stream. A recent hydrogeologic study of the area indicated the following parameter estimates:

$$K_s = 10^{-3} \text{ cm/sec} \qquad\qquad \frac{dh}{dl} = 0.1\% \text{ (gradient)}$$

$$n_t = 0.33 \qquad\qquad a = 2.6 \text{ m (dispersivity)}$$

$$n_e = 0.26 \qquad\qquad B = 1.9 \text{ g/cc}$$

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED __X____

SATURATED _____

Site: _Example No. 1_____   Date of Incident: _____

Location: _____

On Site Coordinator: _____   Agency: _____

Scientific Support
Coordinator: _____   Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS:

C_o = ___1500 mg/l_____

V = ___0.55 cm/day_____

D = ___13.75 cm^2/day_____

k = ___0.004 day^{-1}_____

R = $1 + \frac{B}{\theta} K_d$ = ___1.700_____

K_d = _____0.07 ml/gm_____

B = _____1.5 gm/cm^3_____

θ = _____0.15_____

DATA SOURCES / COMMENTS

Company records

Based on 30 cm/yr recharge rate

Dispersivity = 25 cm, i.e., 10% depth

Company data on compound

Company data on compound

Company soils data

Field capacity for sandy loam

PRELIMINARY CALCULATIONS:

1. $V^* = V/R$ = ___0.324 cm/day___

2. $D^* = D/R$ = ___8.088 cm^2/day___

3. $k^* = k/R$ = ___0.0024 day^{-1}___

4. $\sqrt{V^{*2} + 4D^*k^*}$ = ___0.427___

5	6	7	8	9				10	11	12
				See Footnote # 2				From Nomograph[3]		
x	t	$x/2D^*$	$\sqrt{4D^*t}$	A_1	A_2	B_1	B_2	M_1	M_2	C/C_o	C
10	50	0.62	40.22	-0.06	-0.28	0.46	0.78	1.23	0.43	0.83	1244
30	50	1.85	40.22	-0.19	0.21	1.39	1.28	0.63	0.28	0.46	686
75	50	4.64	40.22	-0.48	1.33	3.48	2.40	0.04	0.03	0.03	52
10	200	0.62	80.44	-0.06	-0.94	0.46	1.19	1.70	0.15	0.93	1388

TABLE 5.1 continued

Sheet __2__ of __2__

NOMOGRAPH WORKSHEET (con't.)

ZONE: UNSATURATED ___X___

SATURATED _____

5	6	7	8	9				10	11	12
x	t	$x/_{2D*}$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]		C
				A_1	A_2	B_1	B_2	M_1	M_2	$C/_{Co}$	
40	200	2.47	80.44	-0.26	-0.57	1.86	1.56	1.22	0.18	0.70	1049
100	200	6.18	80.44	-0.64	0.18	4.64	2.31	0.42	0.16	0.29	434
150	200	9.27	80.44	-0.96	0.80	6.97	2.93	0.10	0.0	0.05	75
50	1000	3.09	179.87	-0.32	-2.10	2.32	2.65	1.45	0.0	0.73	1088
150	1000	9.27	179.87	-0.96	-1.54	6.97	3.21	0.76	0.0	0.38	567
250	1000	15.45	179.87	-1.60	-0.99	11.61	3.77	0.37	0.0	0.19	279

Footnotes:
1. Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. A_1 = Col.7 X (Item 1 - Item 4) = $\frac{x}{2D*}$ $(V* - \sqrt{V*^2 + 4D*k*})$

   A_2 = [Col.5 - Col.6 X Item 4] / Col.8 = $\frac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

   B_1 = Col.7 X (Item 1 + Item 4) = $\frac{x}{2D*}$ $(V* + \sqrt{V*^2 + 4D*k*})$

   B_2 = [Col.5 + (Col.6 X Item 4)] / Col.8 = $\frac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

3. Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

Figure 5.1 Soil Profile Response For Example #1: Demonstrating Fate and Movement of Pollutant.

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED __X__

SATURATED _____

Site: Example No. 1 _____   Date of Incident: _____

Location: _____

On Site Coordinator: _____   Agency: _____

Scientific Support
Coordinator: _____   Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS:

			DATA SOURCES / COMMENTS
C_o =	1500 mg/l		Company records
V =	0.55 cm/day		Based on 30 cm/yr recharge rate
D =	13.75 cm^2/day		Dispersivity = 25 cm, i.e., 10% depth
k =	0.004 day^{-1}		Company data on compound
$R = 1 + \frac{B}{\theta} K_d$ =	1.700		
K_d =	0.07 ml/gm		Company data on compound
B =	1.5 gm/cm^3		Company soils data
θ =	0.15		Field capacity for sandy loam

PRELIMINARY CALCULATIONS:

1. $V^* = V/R$ = 0.324 cm/day

2. $D^* = D/R$ = 8.088 cm^2/day

3. $k^* = k/R$ = 0.0024 day^{-1}

4. $\sqrt{V^{*2} + 4D^*k^*}$ = 0.427

5	6	7	8	9				10	11	12
				See Footnote # 2				From Nomograph[3]		
x	t	$x/2D^*$	$\sqrt{4D^*t}$	A_1	A_2	B_1	B_2	M_1	M_2	C/C_o	C
250	25	15.45	28.44	-1.60	8.42	11.61	9.17	0.0	0.0	0.0	0.0
250	50	15.45	40.22	-1.60	5.69	11.61	6.75	0.0	0.0	0.0	0.0
250	75	15.45	49.26	-1.60	4.43	11.61	5.73	0.0	0.0	0.0	0.0
250	100	15.45	56.88	-1.60	3.64	11.61	5.15	0.0	0.0	0.0	0.0

TABLE 5.2 continued   Sheet ___2___ of ___2_____

Calculated by _____ Date _____

Checked by _____ Date _____

NOMOGRAPH WORKSHEET (con't.)   ZONE: UNSATURATED ____X____

SATURATED _____

5	6	7	8	9				10	11	12
x	t	$x/2D*$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]		C
				A_1	A_2	B_1	B_2	M_1	M_2	C/Co	
250	125	15.45	63.59	-1.60	3.09	11.61	4.77	0.0	0.0	0.0	0.0
250	150	15.45	69.66	-1.60	2.67	11.61	4.51	0.0	0.0	0.0	0.0
250	175	15.45	75.24	-1.60	2.33	11.61	4.32	0.0	0.0	0.0	0.0
250	200	15.45	80.44	-1.60	2.05	11.61	4.17	0.0	0.0	0.0	0.0
250	300	15.45	98.52	-1.60	1.24	11.61	3.84	0.016	0.0	0.008	12.0
250	400	15.45	113.76	-1.60	0.70	11.61	3.70	0.065	0.0	0.03	45.0
250	500	15.45	127.18	-1.60	0.29	11.61	3.65	0.14	0.0	0.07	105.0
250	600	15.45	139.32	-1.60	-0.05	11.61	3.64	0.21	0.0	0.11	165.0
250	800	15.45	160.88	-1.60	-0.57	11.61	3.68	0.32	0.0	0.16	240.0
250	1000	15.45	179.87	-1.60	-0.99	11.61	3.77	0.37	0.0	0.19	285.0
250	1500	15.45	220.29	-1.60	-1.78	11.61	4.05	0.40	0.0	0.20	300.0

Footnotes: 1.   Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. $A_1 = Col.7 \times (Item\ 1 - Item\ 4) = \frac{x}{2D*}(V* - \sqrt{V*^2 + 4D*k*})$

$A_2 = [Col.5 - Col.6 \times Item\ 4] / Col.8 = \frac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

$B_1 = Col.7 \times (Item\ 1 + Item\ 4) = \frac{x}{2D*}(V* + \sqrt{V*^2 + 4D*k*})$

$B_2 = [Col.5 + (Col.6 \times Item\ 4)] / Col.8 = \frac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

3.   Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

Figure 5.2   Example #1:   Time Response at Ground-Water Table

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```
Total aquifer thickness      =  18 m

Effective aquifer thickness  =   6 m
```

Based on the linkage procedures and Equation 3.10 in Section 3.3, the source concentration was calculated as follows:

$$Co = \frac{(300 \text{ mg/l})(.0822 \text{ cm/day})(20 \text{ m})}{(.864 \text{ cm/day})(6m)}$$

$$Co = 95 \text{ mg/l}$$

This calculation assumes a plume width of 20 meters, an effective mixing depth of 6 meters, a recharge rate of 30 cm/yr (0.0822 cm/day), and a ground-water velocity of .864 cm/day (i.e., $V_d = K_s(dh/dl) = (10^{-3}$ cm/sec) (.001)).

Figure 5.2 shows the step function input to the saturated zone used to approximate the actual contaminant outflow from the unsaturated zone. The step function was assumed to begin at day 550 (i.e., 550 days after the beginning of the leak). As discussed in Section 3.3, this beginning time should be varied to evaluate the influence of the step function approximation on the arrival time and response at the discharge or impact point.

Table 5.3 is the worksheet with calculations for the ground-water time response at the stream and Figure 5.3 plots the calculated C/Co values. Figure 5.3 shows that the plume begins to reach the stream between 1000 and 2000 days and reaches a steady-state concentration of 27 mg/l at 6000 days. Note that the time scale is in days after entering the ground water under the site. The total travel time of the spill to the stream would be the above numbers plus 550 days, the beginning day of the step function input to ground water. Note that changing the beginning day of the step function approximation in Figure 5.2 by 200 to 300 days would not have a major impact on the relative arrival time of the plume at the stream. Thus the step function approximation is reasonable.

5.2 EXAMPLE #2: ASSESSMENT OF A PULSE CONTAMINANT SOURCE

Consider a chemical leak similar to Example No. 1 except that the leak is discovered and fixed after 200 days. The following data from Example #1 apply:

```
V    = 0.55 cm/day              B    = 1.5 gm/cm³

D    = 13.75 cm²/day            θ    = 0.22

k    = 0.004 day⁻¹              Co   = 1500 mg/l

K_d  = 0.07 ml/gm               t_o  = 200 days

Depth to water table = 250 cm
```

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED _____

SATURATED ___X___

Site: Example No. 1 _____   Date of Incident: _____

Location: _____

On Site Coordinator: _____   Agency: _____

Scientific Support
Coordinator: _____   Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS:

C_o = 95 (mg/l)

V = 3.32 (cm/day)

D = 860 (cm^2/day)

k = 0.0004 (day^{-1})

$R = 1 + \frac{B}{\theta}K_d$ = 1.06

K_d = 0.01 (ml/gm)

B = 1.9 (gm/cm^3)

θ = 0.33

DATA SOURCES / COMMENTS

Assumes L = 20m, m = 6m

= (10^{-3}cm/sec) (.001) /.26

Dispersivity = 2.6m

Company data, 4.75 yr half-life in G.W

_____

Company data

Recent G.W. Study

Recent G.W. Study

PRELIMINARY CALCULATIONS:

1. $V^* = {}^V/_R$ = 3.132 (cm/day)

2. $D^* = {}^D/_R$ = 811.32 (cm^2/day)

3. $k^* = {}^k/_R$ = 3.774 x 10^{-4} (day^{-1})

4. $\sqrt{V*^2 + 4D*k*}$ = 3.322

5	6	7	8	9				10	11	12
				See Footnote # 2				From Nomograph[3]		
x	t	$^x/_{2D*}$	$\sqrt{4D*t}$	A_1	A_2	B_1	B_2	M_1	M_2	$^C/_{Co}$	C
10000	1000	6.16	1801.5	-1.17	3.71	39.77	7.39	0.0	0.0	0.0	0.0
	2000	6.16	2547.7	-1.17	1.32	39.77	6.53	0.02	0.0	0.01	0.95
	2500	6.16	2848.4	-1.17	0.60	39.77	6.43	0.12	0.0	0.06	5.7
	2800	6.16	3014.4	-1.17	0.23	39.77	6.40	0.23	0.0	0.12	11.44

TABLE 5.3 continued

Sheet __2__ of __2__

Calculated by _____ Date _____

Checked by _____ Date _____

NOMOGRAPH WORKSHEET (con't.)

ZONE: UNSATURATED _____

SATURATED _____X_____

5	6	7	8	9				10	11	12
x	t	$x/2D*$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]		C
				A_1	A_2	B_1	B_2	M_1	M_2	C/C_0	
10000	3000	6.16	3120.2	-1.17	0.01	39.77	6.40	0.31	0.0	0.15	14.25
	3200	6.16	3222.6	-1.17	-0.20	39.77	6.40	0.38	0.0	0.19	18.05
	3500	6.16	3370.2	-1.17	-0.48	39.77	6.42	0.47	0.0	0.23	21.85
	4000	6.16	3602.9	-1.17	-0.91	39.77	6.46	0.56	0.0	0.28	26.60
	6000	6.16	4412.7	-1.17	-2.25	39.77	6.78	0.62	0.0	0.31	29.45

Footnotes:

1. Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. $A_1 = Col.7 \times (Item\ 1 - Item\ 4) = \frac{x}{2D*} (V* - \sqrt{V*^2 + 4D*k*})$

   $A_2 = [Col.5 - Col.6 \times Item\ 4] / Col.8 = \frac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

   $B_1 = Col.7 \times (Item\ 1 + Item\ 4) = \frac{x}{2D*} (V* + \sqrt{V*^2 + 4D*k*})$

   $B_2 = [Col.5 + (Col.6 \times Item\ 4)] / Col.8 = \frac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

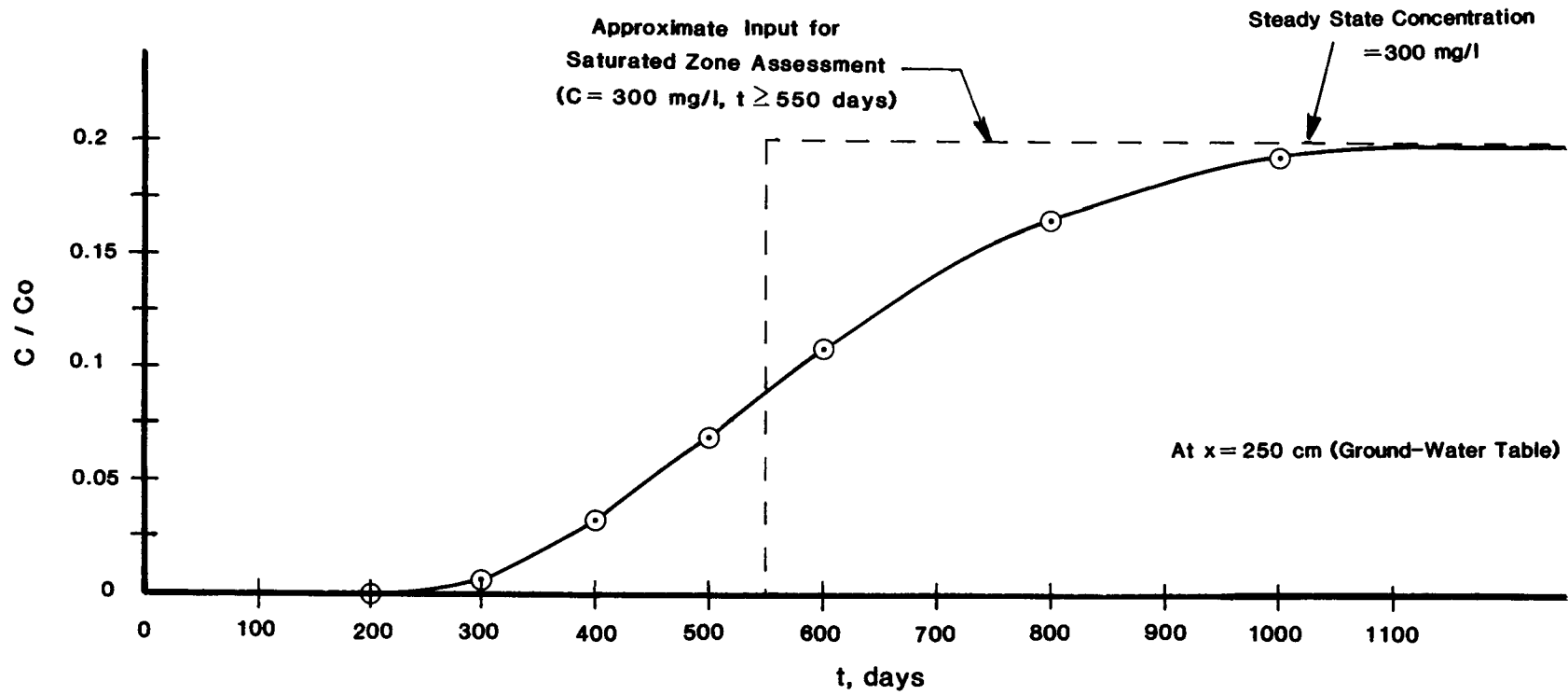3. Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

Figure 5.3 Example No. 1: Time Response At The Stream (x=100m)

A time response is evaluated to assess the chemical concentration as it reaches the ground-water table. The calculations are shown in worksheets, Tables 5.4 and 5.5, according to the procedures stated in Section 3.1.4. The response is evaluated at 250 cm, the estimated depth to ground water. The reader should note that concentrations are evaluated at times which differ by one pulse period (i.e. 200 days). This procedure can help to minimize the number of calculations required, since values of C/Co in column 5 of Table 5.5 can be directly entered by shifting the values in column 4 down to the appropriate row. The results are plotted in Figure 5.4 indicating a bell-shape time response curve. The plot indicates that the plume begins to arrive at the ground-water table in approximately 200 days, with a peak concentration of 120 mg/l (C/Co = 0.08) occurring in about 600 days. It also indicates that the plume would completely enter the ground water in about 1300 - 1400 days.

The primary purpose of the unsaturated zone analysis is to obtain a concentration-time response at the ground-water table, so that the bell-shape time response curve can be approximated by a pulse input and applied as a pollutant source for the saturated zone assessment. Following the same approximation procedures discussed in Section 3.3 and using the same parameter values from Example #1, the pulse concentration of 105 mg/l shown in Figure 5.4 produces a Co = 33.0 mg/l for the saturated zone assessment. Tables 5.6 and 5.7 show the worksheet calculations for the time response at the stream, which is plotted in Figure 5.5. Note that the arrival times for the pulse and step function inputs are similar, but that the maximum concentration for the pulse input is only 3.4 mg/l at 3400 days after the spill while the step function (Figure 5.3) produced 29 mg/l at 6550 days.

TABLE 5.4 TIME RESPONSE FOR <u>PULSE INPUT</u>
TO UNSATURATED ZONE - STANDARD
WORKSHEET

Sheet __1__ of __2__

Calculated by _____ Date _____

Checked by _____ Date _____

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED __X__

SATURATED _____

Site: __Example No. 2__   Date of Incident: _____

Location: _____

On Site Coordinator: _____   Agency: _____

Scientific Support
Coordinator: _____   Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS:

		DATA SOURCES / COMMENTS
C_o =	1500 mg/l	Company records
V =	0.55 cm/day	Based on 30 cm/yr recharge rate
D =	13.75 cm^2/day	Dispersivity = 25 cm, i.e., 10% depth
k =	0.004 day^{-1}	Company data on compound
$R = 1 + \frac{B}{\theta} K_d$ =	1.700	
K_d =	0.07 ml/gm	Company data on compound
B =	1.5 gm/cm^3	Company soils data
θ =	0.15	Field capacity for sandy loam

PRELIMINARY CALCULATIONS:

1. $V^* = V/R$ = __0.324__ cm/day

2. $D^* = D/R$ = __8.088__ cm^{-2}/day

3. $k^* = k/R$ = __0.0024__ day^{-1}

4. $\sqrt{V^{*2} + 4D^*k^*}$ = __0.427__

5	6	7	8	9				10	11	12
				See Footnote # 2				From Nomograph[3]		
x	t	$x/2D^*$	$\sqrt{4D^*t}$	A_1	A_2	B_1	B_2	M_1	M_2	C/C_o	C
250	100	15.45	56.88	-1.60	3.64	11.61	5.15	0.0	0.0	0.0	0.0
250	200	15.45	80.44	-1.60	2.05	11.61	4.17	0.0	0.0	0.0	0.0
250	300	15.45	98.52	-1.60	1.24	11.61	3.84	0.016	0.0	0.008	12.0
250	400	15.45	113.76	-1.60	0.70	11.61	3.70	0.065	0.0	0.03	45.0

TABLE 5.4 continued

NOMOGRAPH WORKSHEET (con't.)

ZONE: UNSATURATED ___X___

SATURATED _____

5	6	7	8	9				10		11	12
x	t	$x/_{2D*}$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]			C
				A_1	A_2	B_1	B_2	M_1	M_2	$C/_{Co}$	
250	500	15.45	127.18	-1.60	0.29	11.61	3.65	0.14	0.0	0.07	105.0
250	600	15.45	139.32	-1.60	-0.05	11.61	3.64	0.21	0.0	0.11	165.0
250	800	15.45	160.88	-1.60	-0.57	11.61	3.68	0.32	0.0	0.16	240.0
250	1000	15.45	179.87	-1.60	-0.99	11.61	3.77	0.37	0.0	0.19	285.0
250	1200	15.45	197.03	-1.60	-1.33	11.61	3.87	0.39	0.0	0.20	300.0

Footnotes:

1. Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. $A_1 = Col.7 \ X \ (Item\ 1 - Item\ 4) = \frac{x}{2D*}(V* - \sqrt{V*^2 + 4D*k*})$

$A_2 = [Col.5 - Col.6 \ X \ Item\ 4] / Col.8 = \frac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

$B_1 = Col.7 \ X \ (Item\ 1 + Item\ 4) = \frac{x}{2D*}(V* + \sqrt{V*^2 + 4D*k*})$

$B_2 = [Col.5 + (Col.6 \ X \ Item\ 4)] / Col.8 = \frac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

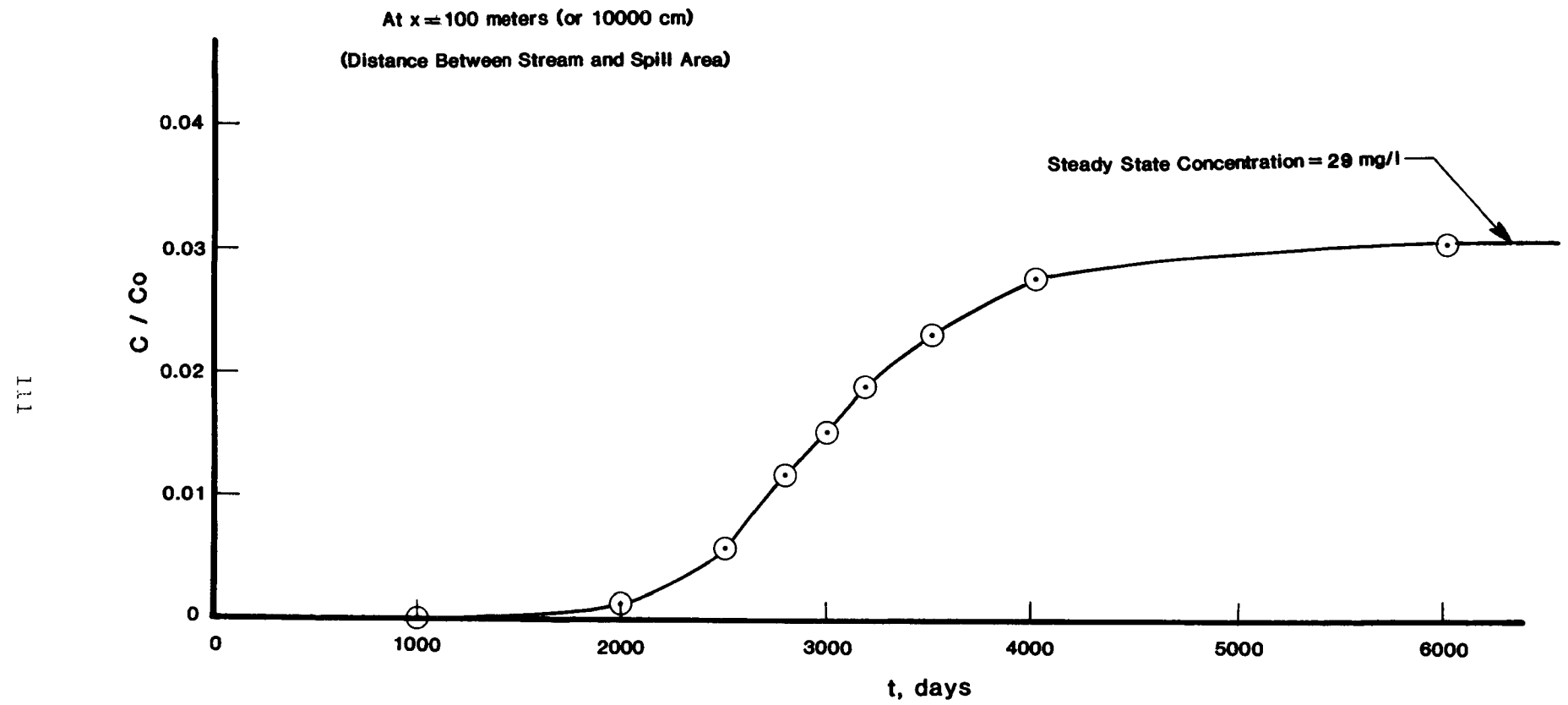3. Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

SUPPLEMENTARY WORKSHEET FOR PULSE INPUT ASSESSMENT

ZONE: UNSATURATED __X__

to = __200 days__ ,   Co = __1500 mg/l__   SATURATED _____

			CONTINUOUS INPUT ASSESSMENT (From Worksheet)		PULSE ASSESSMENT	
					$Col.4, t \le to$ $Col.4-5, t > to$	$Co \times Col. 6$
1	2	3	4	5	6	7
x	t	t - to	$C/_{Co}(t)$	$C/_{Co}(t - to)$	$C/_{Co}(t)$	C
250	200	0	0.0	0.0	0.0	0.0
250	300	100	0.008	0.0	0.008	12.0
250	400	200	0.03	0.0	0.03	45.0
250	500	300	0.07	0.008	0.06	93.0
250	600	400	0.11	0.03	0.08	120.0
250	800	600	0.16	0.11	0.05	75.0
250	1000	800	0.19	0.16	0.03	45.0
250	1200	1000	0.20	0.19	0.01	15.0

Figure 5.4 Example #2; Time Response at Ground-Water Table. (Pulse Input)

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED _____

SATURATED ____X____

Site: __Example No. 2__   Date of Incident: _____

Location: _____

On Site Coordinator: _____   Agency: _____

Scientific Support
Coordinator: _____   Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS:

C_o = __33__ (mg/l)

V = __3.32__ (cm/day)

D = __860__ (cm^2/day)

k = __0.0004__ (day^{-1})

$R = 1 + \frac{B}{\theta} K_d$ = __1.06__

K_d = __0.01__ (ml/gm

B = __1.9__ (gm/cm^3)

θ = __0.26__

DATA SOURCES / COMMENTS

Results from pulse input linkage

= (10^{-3}cm/sec) (.001) /.26

Dispersivity = 2.6m

Company data, 4.75 yr half-life in G.W.

Company data

Recent G.W. Study

Recent G.W. Study

PRELIMINARY CALCULATIONS:

1. $V^* = V/R$ = __3.132__ (cm/day)

2. $D^* = D/R$ = __811.32__ (cm^2/day)

3. $k^* = k/R$ = __3.774 x 10^{-4} (day^{-1})__

4. $\sqrt{V^{*2} + 4D^* k^*}$ = __3.322__

5	6	7	8	9					10	11	12
				See Footnote # 2					From Nomograph[3]		
x	t	$x/2D^*$	$\sqrt{4D^* t}$	A_1	A_2	B_1	B_2		M_1	M_2	C/C_o	C
10000	1400	6.16	2131.5	-1.17	2.51	39.77	6.87	0.0	0.0	0.0	0.0
10000	2000	6.16	2547.7	-1.17	1.32	39.77	6.53	0.02	0.0	0.01	.33
10000	2600	6.16	2904.8	-1.17	0.47	39.77	6.42	0.16	0.0	0.08	2.64
10000	3200	6.16	3222.6	-1.17	-0.20	39.77	6.40	0.38	0.0	0.19	6.27

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TABLE 5.6 continued

Sheet ___2___ of ___2___

NOMOGRAPH WORKSHEET (con't.)

ZONE: UNSATURATED _____

SATURATED ____X____

5	6	7	8	9				10	11	12
x	t	$x/_{2D*}$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]		C
				A_1	A_2	B_1	B_2	M_1	M_2	$C/_{Co}$	
10000	3800	6.16	3511.7	-1.17	-0.75	39.77	6.44	0.53	0.0	0.27	8.91
10000	4400	6.16	3778.8	-1.17	-1.22	39.77	6.51	0.59	0.0	0.30	9.90
10000	5000	6.16	4028.2	-1.17	-1.64	39.77	6.61	0.61	0.0	0.31	10.23
10000	5600	6.16	4263.1	-1.17	-2.02	39.77	6.71	0.62	0.0	0.31	10.23
10000	1700	6.16	2348.8	-1.17	1.85	39.77	6.66	0.0	0.0	0.0	0.0
	2300	6.16	2732.1	-1.17	0.86	39.77	6.46	0.07	0.0	0.03	.99
	2900	6.16	3067.8	-1.17	0.12	39.77	6.40	0.27	0.0	0.13	4.29
	3500	6.16	3370.2	-1.17	-0.48	39.77	6.42	0.47	0.0	0.23	7.59
	4100	6.16	3647.7	-1.17	-0.99	39.77	6.48	0.57	0.0	0.29	9.57

Footnotes: 1. Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. A_1 = Col.7 X (Item 1 - Item 4) = $\frac{x}{2D*}$ $(V* - \sqrt{V*^2 + 4D*k*})$

A_2 = [Col.5 - Col.6 X Item 4] / Col.8 = $\frac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

B_1 = Col.7 X (Item 1 + Item 4) = $\frac{x}{2D*}$ $(V* + \sqrt{V*^2 + 4D*k*})$

B_2 = [Col.5 + (Col.6 X Item 4)] / Col.8 = $\frac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

3. Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

SUPPLEMENTARY WORKSHEET FOR PULSE INPUT ASSESSMENT

ZONE: UNSATURATED _____

to = __600 days__ ,   Co = ___33 mg/l___   **SATURATED __X__**

			CONTINUOUS INPUT ASSESSMENT (From Worksheet)		PULSE ASSESSMENT	
					Col.4, t ≤ to Col.4-5, t > to	Co X Col. 6
1	2	3	4	5	6	7
x	t	t - to	C/C_o (t)	C/C_o (t - to)	C/C_o (t)	C
10000	2000	1400	0.01	0.0	0.01	.33
	2600	2000	0.08	0.01	0.07	2.31
	3200	2600	0.19	0.08	0.11	3.63
	3800	3200	0.27	0.19	0.08	2.64
	4400	3800	0.30	0.27	0.03	0.99
	5000	4400	0.31	0.30	0.01	0.33
	5600	5000	0.31	0.31	0.0	0.0
10000	2300	1700	0.03	0.0	0.03	0.99
	2900	2300	0.13	0.03	0.10	3.30
	3500	2900	0.23	0.13	0.10	3.30
	4100	3500	0.29	0.23	0.06	1.98

At x = 100 meters (Distance Between Stream and Spill Area)

C = 3.6 mg/l

Figure 5.5   Example #2:   Time Response At The Stream   (x=100m)

SECTION 6

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APPENDICES

A. U.S. SOIL CONSERVATION SERVICE RUNOFF ESTIMATION METHOD

B. GLOSSARY OF TERMS

C. BLANK WORKSHEETS AND ENLARGED NOMOGRAPHS FOR RAPID
   ASSESSMENT PROCEDURES

APPENDIX A

U.S. SOIL CONSERVATION SERVICE
RUNOFF ESTIMATION PERIOD

(taken directly from: Stewart et al., 1976)

SIMULATION OF DAILY POTENTIAL DIRECT RUNOFF

INTRODUCTION

The amount and seasonal distribution of direct runoff was estimated to assess potential transport of pesticides and nutrients. The effects of some land management practices on direct runoff were also estimated. Hydrologists have developed several rainfall-runoff models of various degrees of complexity for making these estimates. The more physically realistic models are quite complicated and require a great deal of input information and computer time. The national scope of this report and the severe time constraints involved dictated the use of a rather simple method of estimating runoff from rainfall. Any input information required must also be readily available. After considering several possibilities, we decided to use the Soil Conservation Service procedure for estimating direct runoff from storm rainfall (4).

THE SOIL CONSERVATION SERVICE PROCEDURE FOR ESTIMATING DIRECT RUNOFF FROM STORM RAINFALL

The Soil Conservation Service procedure for estimating direct runoff from storm rainfall (sometimes called the SCS curve number method) was designed to use the most generally available rainfall data: total daily rainfall. For this reason rainfall intensity is largely ignored. The basic relationship is the equation:

$$Q = \frac{(P-I_a)^2}{(P-I_a) + S} \quad ; P \geq I_a \quad (1)$$

where

Q = runoff in inches
P = rainfall in inches
I_a = initial abstraction in inches
S = potential maximum retention plus initial abstraction.

The initial abstraction before runoff begins is considered to consist mainly of interception, infiltration and surface storage. Utilizing limited data from small experimental watersheds, the following empirical relationship was developed:

$$I_a = (0.2)S. \quad (2)$$

Substituting this relationship into equation (1) gives

$$Q = \frac{(P-0.2S)^2}{P+0.8S} \quad , P \geq (0.2) S , \quad (3)$$

which is the rainfall-runoff relation used in the SCS method.

The parameter CN (runoff curve number of hydrologic soil-cover complex number) is defined in terms of the parameter S as:

$$CN = \frac{1000}{S+10} \quad (4)$$

Note that runoff equals rainfall when $S = 0$ and $CN = 100$.

The potential maximum retention, S, and therefore the runoff curve number are related to soil surface and profile properties, the vegetative cover, management practices, and the soil water content on the day of the storm. Solutions of equation (3) are shown as a family of curves in Fig. 1.

Soil water content on the day of the storm is accounted for by an Antecedent Moisture Condition (AMC) determined by the total rainfall in the 5-day period preceding the storm.

Three AMC groups have been established with the boundaries between groups dependent upon the time of year as shown in Table 1.

The seasonal difference in the AMC groupings is an attempt to account for the greater evapotranspiration between storms during the growing season.

The different infiltration characteristics of soils are accounted for by classifying soils into four groups based

HYDROLOGY: SOLUTION OF RUNOFF EQUATION $Q = \frac{(P-0.2S)^2}{P+0.8S}$

P = 0 to 12 inches
Q = 0 to 8 inches

$Q = \frac{(P-I_a)^2}{P-I_a+S}$ With $P \geq I_a$; $S \geq I_a + F$; and $F = P - I_a - Q$

Curves on this sheet are for the case $I_a = 0.2S$, so that

$Q = \frac{(P-0.2S)^2}{P+0.8S}$

Rainfall (P)
RUNOFF (Q)
Rate
F
Time
initial abstraction I_a
Infiltration curve

CURVE NUMBER = $\frac{1000}{10+S}$

100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20

DIRECT RUNOFF (Q) IN INCHES

RAINFALL (P) IN INCHES

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REFERENCE
Mockus, Victor; Estimating direct runoff amounts from storm rainfall:
Central Technical Unit, October 1955

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SOIL CONSERVATION SERVICE
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Figure 1.–Solutions of Eq. 3. [From SCS National Engineering Handbook (4)]

AMC group	Total 5-day antecedent rainfall	
	Dormant season	Growing season
	inches	inches
I	<0.5	<1.4
II	0.5 - 1.1	1.4 - 2.1
III	>1.1	>2.1

[1] From SCS National Engineering Handbook (4).

upon the minimum rate of infiltration obtained for a bare soil after prolonged wetting. The influences of both the surface and the profile of a soil are included. The hydrologic soil groups as defined by SCS soil scientists in the National Engineering Handbook are:

A. (Low runoff potential). Soils having high infiltration rates even when thoroughly wetted and consisting chiefly of deep, well to excessively drained sands or gravels. These soils have a high rate of water transmission.

B. Soils having moderate infiltration rates when thoroughly wetted and consisting chiefly of moderately deep to deep, moderately well to well drained soils with moderately fine to moderately coarse textures. These soils have a moderate rate of water transmission.

C. Soils having slow infiltration rates when thoroughly wetted and consisting chiefly of soils with a layer that impedes downward movement of water, or soils with moderately fine to fine texture. These soils have a slow rate of water transmission.

D. (High runoff potential). Soils having very slow infiltration rates when thoroughly wetted and consisting chiefly of clay soils with a high swelling potential, soils with a permanent high water table, soils with a claypan or clay layer at or near the surface, and shallow soils over nearly impervious material. These soils have a very slow rate of water transmission.

The SCS has classified over 9,000 soils in the United States and Puerto Rico according to the above scheme. A sample from the extensive table in the SCS National Engineering Handbook is shown in Table 2. Rainfall-runoff data from small watersheds or infiltrometer plots were used to make the classifications where such data were available, but most are based on the judgement of soil scientists and correlators who used physical properties of the soils in making the assignments.

The interaction of hydrologic soil group (soil) and land use and treatment (cover) is accounted for by assigning a runoff curve number for average soil moisture condition (AMC II) to important soil cover complexes for the fallow period and the growing season. Rainfall-runoff data for single soil cover complex watersheds and plots were analyzed to provide a basis for making these assignments. Average runoff curve numbers for several soil-cover complexes are shown in Table 3. Average runoff curve numbers (AMC II) are for the average soil moisture conditions. AMC I has the lowest runoff potential. AMC III has the highest runoff potential. Under this condition the watershed is practically saturated from antecedent rains. Appropriate curve numbers for AMC I and III based upon the curve number for AMC II are shown in Table 4.

Curve numbers for a "good hydrologic condition" were used in the potential direct runoff simulations. "Hydrologic condition" refers to the runoff potential of a particular cropping practice. A row crop in good hydrologic condition will have higher infiltration rates and, consequently, less direct runoff than the same crop in poor hydrologic condition. Good hydrologic condition seemed an appropriate description of corn under modern management practices.

Seasonal variation not accounted for by the seasonal dependency of the AMC classes is included by varying the average moisture condition curve number according to the stages of growth of a particular crop. For the simulations reported here, with straight row corn as the index crop, the average (AMC II) curve number was set equal to that for fallow for the period from March 1 until the average emergence date for corn. Emergence dates were assumed to be 2 weeks after the average planting date reported by the USDA (5). During the growing season, AMC II curve numbers for each day were calculated by the following equation:

$$CN_i = F - \frac{C_i}{C_{ave}} (F - CN_{ave}) \qquad (5)$$

where

CN_i = the curve number for the ith day for AMC II.

F = fallow curve number.

C_i = crop coefficient for the ith day. $C_i \leq 1$.

C_{ave} = average crop coefficient for the growing season.

CN_{ave} = average growing season curve number for AMC II.

The crop coefficients C_i are defined as the ratio of the crop evapotranspiration to potential evapotranspiration for a given day when soil water is not limiting. Crop

Table 2.—Soil names and hydrologic classifications[1] (Sample)

Soil	HSG	Soil	HSG	Soil	HSG	Soil	HSG	Soil	HSG
AABERG	C	AHL	C	ALMY	B	ANLAUF	C	AROOSTOOK	C
AASTAD	B	AHLSTROM	C	ALOHA	C	ANNABELLA	B	AROSA	B
ABAC	O	AHMEER	B	ALONSO	B	ANNANDALE	C	ARP	C
ABAJU	C	AHOLT	D	ALOVAR	C	ANNISTON	B	ARRINGTON	B
ABBOTT	D	AHTANUM	C	ALPENA	B	ANOKA	A	ARRITOLA	D
ABBOTTSTOWN	C	AHWAHNEE	C	ALPHA	C	ANONES	C	ARROLIME	C
ABCAL	D	AIBONITO	C	ALPUN	B	ANSARI	D	ARRON	D
ABEGG	B	AIKEN	B/C	ALPOWA	B	ANSEL	B	ARROW	B
ABELA	B	AIKMAN	D	ALPS	C	ANSELMO	A	ARROWSMITH	B
ABELL	B	AILEY	B	ALSEA	B	ANSON	B	ARROYO SECO	B
ABERDEEN	D	AINAKEA	B	ALSPAUGH	C	ANTELOPE SPRINGS	C	ARTA	C
ABES	D	AIRMONT	C	ALSTAD	B	ANTERO	C	ARTOIS	D
ABILENE	-	AIROTSA	B	ALSTOWN	B	ANT FLAT	C	ARVADA	C
ABINGTON	D	AIRPORT	D	ALTAMONT	D	ANTHO	B	ARVANA	C
ABIQUA	C	AITS	B	ALTAVISTA	C	ANTHONY	B	ARVESON	D
ABU	B/C	AJO	C	ALTDORF	D	ANTIGO	B	ARVILLA	B
ABOR	D	AKAKA	A	ALTMAR	B	ANTILON	B	ARZELL	C
ABRA	C	AKASKA	B	ALTU	C	ANTIOCH	D	ASA	B
ABRAHAM	B	AKELA	C	ALTOGA	C	ANTLER	C	ASBURY	B
ABSAROKEE	C	ALADDIN	B	ALTON	B	ANTOINE	C	ASCALON	B
ABSCOTA	B	ALAE	A	ALTUS	B	ANTROBUS	B	ASCHOFF	B
ABSHER	D	ALAELOA	B	ALTVAN	B	ANTY	B	ASHBY	C
ABSTED	U	ALAGA	A	ALUM	B	ANVIK	B	ASHCROFT	B
ACACIO	C	ALAKAI	U	ALUSA	D	ANWAY	B	ASHDALE	B
ACADEMY	-	ALAMA	B	ALVIN	B	ANZA	B	ASHE	B
ACADIA	O	ALAMANCE	B	ALVIRA	C	ANZIANO	C	ASHKUM	C
ACANA	D	ALAMC	D	ALVISO	D	APACHE	D	ASHLAR	B
ACASCO	D	ALAMOSA	C	ALVOR	C	APAKUIE	A	ASHLEY	A
ACEITUNAS	B	ALAPAHA	D	AMADOR	D	APISHAPA	C	ASH SPRINGS	C
ACEL	J	ALAPAI	A	AMAGON	D	APISON	B	ASHTON	B
ACKER	B	ALBAN	B	AMALU	D	APOPKA	A	ASHUE	B
ACKMEN	B	ALBANO	D	AMANA	B	APPIAN	C	ASHUELOT	C
ACME	C	ALBANY	C	AMARGOSA	D	APPLEGATE	C	ASHWOOD	C
ACO	B	ALBATON	D	AMARILLO	B	APPLETON	C	ASKEW	C
ACULITA	B	ALBEE	C	AMASA	B	APPLING	B	ASO	C
ACUNA	C	ALBEMARLE	B	AMBERSON		APRON	B	ASOTIN	C
ACOVE	C	ALBERTVILLE	C	AMBOY	C	APT	C	ASPEN	B
ACKEE	C	ALBIA	C	AMBRAW	C	APTAKISIC	B	ASPERMONT	B
ACRELANE	C	ALBION	B	AMEDEE	A	ARABY	A	ASSINNIBOINE	
ACTUN	B	ALBRIGHTS	C	AMELIA	B	ARADA	C	ASSUMPTION	B
ACUFF	B	ALCALDE	C	AMENIA	B	ARANSAS	D	ASTATULA	A
ACWORTH	B	ALCESTER	B	AMERICUS	A	ARAPIEN	C	ASTOR	A/D
ALY	C	ALGUA	B	AMES	C	ARAVE	D	ASTORIA	B
ADA	B	ALCONA	B	AMESHA	B	ARAVETON	B	ATASCADERO	C
ADAIR	D	ALCOVA	B	AMHERST	C	ARBELA	C	ATASCOSA	D
ADAMS	A	ALDA	C	AMITY	C	ARBONE	B	ATCO	B
ADAMSON	B	ALDAX	D	AMMON	B	ARBOR	B	ATENCIO	B
ADAMSTOWN		ALDEN	D	AMOLE	C	ARBUCKLE	B	ATEPIC	D
ADAMSVILLE	C	ALDER	B	AMOR	B	ARCATA	B	ATHELWOLD	B
ACATON	D	ALDERDALE	C	AMOS	C	ARCH	B	ATHENA	B
ADAVEN	D	ALDERWOOD	C	AMSDEN	B	ARCHABAL	B	ATHENS	B
ADDIELOU	C	ALDINO	C	AMSTERDAM	B	ARCHER	C	ATHERLY	B
ADDISON	D	ALDWELL	C	AMTOFT	D	ARCHIN	C	ATHERTON	B/D
ADDY	C	ALEKNAGIK	B	AMY	D	ARCO	B	ATHMAR	C
ADE	A	ALEMEDA	C	ANACAPA	B	ARCOLA	B	ATHOL	B
ADEL	A	ALEX	B	ANAHUAC	D	ARD	C	ATKINSON	B
ADELAIDE	D	ALEXANDRIA	C	ANAHITE	D	ARDEN	B	ATLAS	D
ADELANTO	B	ALEXIS	B	ANAPRA	B	ARDENVOIR	B	ATLEE	C
ADELINO	B	ALFORD	B	ANASAZI	B	ARGILLA	C	ATHORE	B/D
ADELPHIA	C	ALGANSEE	B	ANATONE	D	AREDALE	B	ATOKA	C
ADENA	C	ALGERITA	B	ANAVERDE	B	ARENA	C	ATON	B
ADGER	D	ALGIERS	C/D	ANAWALT	D	ARENALES	A	ATRYPA	C
ADILIS	A	ALGOMA	B/D	ANCHO	B	ARENOTSVILLE	B	ATSION	C
ADIRONDACK		ALHAMBRA	B	ANCHORAGE	A	ARENOSA	A	ATTERBERRY	B
ADIV	B	ALICE	A	ANCHOR BAY	D	ARENZVILLE	B	ATTEWAN	A
ADJUNTAS	C	ALICEL	B	ANCHOR POINT	D	ARGONAUT	D	ATTICA	B
ADKINS	B	ALICIA	B	ANCLOTE	D	ARGUELLO	B	ATTLEBORO	
ADLER	C	ALIDA	B	ANCO	C	ARGYLE	B	ATWATER	B
ADOLPH	D	ALIKCHI	B	ANDERLY	C	ARIEL	C	ATWELL	C/D
ADRIAN	A/D	ALINE	A	ANDERS	C	ARIZO	A	ATWOOD	B
AENEAS	B	ALKO	D	ANDERSON	B	ARKABUTLA	C	AUBBEENAUBBEE	B
AETNA	B	ALLAGASH	B	ANDES	C	ARKPORT	B	AUBERRY	B
AFTON	D	ALLARD	B	ANDORINIA	C	ARLAND	B	AUBURN	C/D
AGAR	B	ALLEGHENY	B	ANDOVER	D	ARLE	B	AUBURNDALE	D
AGASSIZ	D	ALLEMANDS	D	ANDREEN	B	ARLING	B	AUDIAN	B
AGATE	D	ALLEN	B	ANDREESON	C	ARLINGTON	C	AU GRES	C
AGAWAM	B	ALLENWALE	C	ANDRES	B	ARLOVAL	C	AUGSBURG	B
AGENCY	C	ALLENS PARK	B	ANDREWS	C	ARMAGH	D	AUGUSTA	C
AGER	U	ALLENSVILLE	C	ANED	D	ARMIJO	D	AULD	D
AGNER	B	ALLENTINE	D	ANETH	A	ARMINGTON	D	AURA	B
AGNEW	B/C	ALLENWOOD	B	ANGELICA	D	ARMO	B	AURORA	C
AGNOS	B	ALLESSIO	B	ANGELINA	B/D	ARMOUR	B	AUSTIN	C
AGUA	B	ALLEY	C	ANGELO	C	ARMSTER	C	AUSTWELL	D
AGUADILLA	A	ALLIANCE	B	ANGIE	C	ARMSTRONG	D	AUXVASSE	D
AGUA DULCE	C	ALLIGATOR	D	ANGLE	A	ARMUCHEE	D	AUZQUI	B
AGUA FRIA	B	ALLIS	O	ANGLEN	B	ARNEGARD	B	AVA	C
AGUALT	B	ALLISON	C	ANGOLA	C	ARNHART	C	AVALANCHE	B
AGUEDA	B	ALLOUEZ	C	ANGOSTURA	B	ARNHEIM	C	AVALON	B
AGUILITA	B	ALLGWAY		ANHALT	D	ARNO	D	AVERY	B
AGUIRRE	U	ALMAC	B	ANIAK	D	ARNOLD	B	AVON	C
AGUSTIN	B	ALMENA	C	ANITA	D	ARNOT	C/D	AVONBURG	D
AMATONE	D	ALMONT	D	ANKENY	A	ARNY	A	AVONDALE	E

NOTES   A BLANK HYDROLOGIC SOIL GROUP INDICATES THE SOIL GROUP HAS NOT BEEN DETERMINED
TWO SOIL GROUPS SUCH AS B/C INDICATES THE DRAINED/UNDRAINED SITUATION

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[1] From SCS National Engineering Handbook (4).

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Table 3.- Runoff curve numbers for hydrologic soil-cover complexes[1]

(Antecedent moisture condition II, and I_a = 0.2 S)

Land use	Cover Treatment or practice	Hydrologic condition	Hydrologic soil group A	B	C	D
Fallow	Straight row	----	77	86	91	94
Row crops	"	Poor	72	81	88	91
	"	Good	67	78	85	89
	Contoured	Poor	70	79	84	88
	"	Good	65	75	82	86
	" and terraced	Poor	66	74	80	82
	" " "	Good	62	71	78	81
Small grain	Straight row	Poor	65	76	84	88
	"	Good	63	75	83	87
	Contoured	Poor	63	74	82	85
	"	Good	61	73	81	84
	" and terraced	Poor	61	72	79	82
	" " "	Good	59	70	78	81
Close-seeded legumes[2]	Straight row	Poor	66	77	85	89
or rotation meadow	" "	Good	58	72	81	85
	Contoured	Poor	64	75	83	85
	"	Good	55	69	78	83
	" and terraced	Poor	63	73	80	83
	" " "	Good	51	67	76	80
Pasture or range		Poor	68	79	86	89
		Fair	49	69	79	84
		Good	39	61	74	80
	Contoured	Poor	47	67	81	88
	"	Fair	25	59	75	83
	"	Good	6	35	70	79
Meadow		Good	30	58	71	78
Woods		Poor	45	66	77	83
		Fair	36	60	73	79
		Good	25	55	70	77
Farmsteads		----	59	74	82	86
Roads (dirt)[3]		----	72	82	87	89
(hard surface)[3]		----	74	84	90	92

[1] From SCS National Engineering Handbook (4).
[2] Close-drilled or broadcast.
[3] Including right-of-way.

Table 4.-Curve numbers (CN) and constants for the case $I_a = 0.2S$ [1]

1	2	3	4	5
CN for condition II	CN for conditions		S values [2]	Curve [2] starts where P =
	I	III	(inches)	(inches)
100	100	100	0	0
99	97	100	.101	.02
98	94	99	.204	.04
97	91	99	.309	.06
96	89	99	.417	.08
95	87	98	.526	.11
94	85	98	.638	.13
93	83	98	.753	.15
92	81	97	.870	.17
91	80	97	.989	.20
90	78	96	1.11	.22
89	76	96	1.24	.25
88	75	95	1.36	.27
87	73	95	1.49	.30
86	72	94	1.63	.33
85	70	94	1.76	.35
84	68	93	1.90	.38
83	67	93	2.05	.41
82	66	92	2.20	.44
81	64	92	2.34	.47
80	63	91	2.50	.50
79	62	91	2.66	.53
78	60	90	2.82	.56
77	59	89	2.99	.60
76	58	89	3.16	.63
75	57	88	3.33	.67
74	55	88	3.51	.70
73	54	87	3.70	.74
72	53	86	3.89	.78
71	52	86	4.08	.82
70	51	85	4.28	.86
69	50	84	4.49	.90
68	48	84	4.70	.94
67	47	83	4.92	.98
66	46	82	5.15	1.03
65	45	82	5.38	1.08
64	44	81	5.62	1.12
63	43	80	5.87	1.17
62	42	79	6.13	1.23
61	41	78	6.39	1.28

1	2	3	4	5
CN for condition II	CN for conditions		S values [2]	Curve [2] starts where P =
	I	III	(inches)	(inches)
60	40	78	6.67	1.33
59	39	77	6.95	1.39
58	38	76	7.24	1.45
57	37	75	7.54	1.51
56	36	75	7.86	1.57
55	35	74	8.18	1.64
54	34	73	8.52	1.70
53	33	72	8.87	1.77
52	32	71	9.23	1.85
51	31	70	9.61	1.92
50	31	70	10.0	2.00
49	30	69	10.4	2.08
48	29	68	10.8	2.16
47	28	67	11.3	2.26
46	27	66	11.7	2.34
45	26	65	12.2	2.44
44	25	64	12.7	2.54
43	25	63	13.2	2.64
42	24	62	13.8	2.76
41	23	61	14.4	2.88
40	22	60	15.0	3.00
39	21	59	15.6	3.12
38	21	58	16.3	3.26
37	20	57	17.0	3.40
36	19	56	17.8	3.56
35	18	55	18.6	3.72
34	18	54	19.4	3.88
33	17	53	20.3	4.06
32	16	52	21.2	4.24
31	16	51	22.2	4.44
30	15	50	23.3	4.66
25	12	43	30.0	6.00
20	9	37	40.0	8.00
15	6	30	56.7	11.34
10	4	22	90.0	18.00
5	2	13	190.0	38.00
0	0	0	infinity	infinity

[1] From SCS National Engineering Handbook (4).
[2] For CN in Column 1.

APPENDIX B

GLOSSARY OF TERMS

(Source: The Water Information Center,
Port Washington, N.Y.)

GLOSSARY

Acidization - The process of forcing acid through a well screen or into the limestone, dolomite, or sandstone making up the wall of a borehole. The general objective of acidization is to clean incrustations from the well screen or to increase permeability of the aquifer materials surrounding a well by dissolving and removing a part of the rock constituents.

Anion - An atom or radical carrying a negative charge.

Annular Space (Annulus) - The space between casing or well screen and the wall of the drilled hole or between drill pipe and casing.

Aquiclude - A saturated, but poorly permeable bed, formation, or group of formations that impedes ground-water movement and does not yield water freely to a well or spring. However, an aquiclude may transmit appreciable water to or from adjacent aquifers, and where sufficiently thick, may constitute an important ground-water storage unit.

Aquifer - A geologic formation, group of formations, or part of a formation that is capable of yielding a significant amount of water to a well or spring.

Aquitard - Used synonymously with aquiclude.

Artesian - The occurrence of ground water under greater than atmospheric pressure.

Artesian (Confined) Aquifer - An aquifer bounded by aquicludes and containing water under artesian conditions.

Artificial Recharge - The addition of water to the ground-water reservoir by activities of man.

Backwashing - The surging effect or reversal of water flow in a well. Backwashing removes fine-grained material from the formation surrounding the borehole and, thus, can enhance well yield.

Barrier Well - A pumping well used to intercept a plume of contaminated ground water. Also a recharge well that delivers water to or in the vicinity of a zone of contamination under sufficient head to prevent the further spreading of the contaminant.

Base Flow - The flow of streams composed solely of ground-water discharge.

Biochemical Oxygen Demand (BOD) - A measure of the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present in water.

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Borehole - An uncased drilled hole.

Brine - A concentrated solution, especially of chloride salts.

Casing - Steel or plastic pipe or tubing that is welded or screwed together and lowered into a borehole to prevent entry of loose rock, gas, or liquid or to prevent loss of drilling fluid into porous, cavernous, or fractured strata.

Cation - An atom or radical carrying a positive charge.

Chemical Oxygen Demand (COD) - The amount of oxygen, expressed in parts per million, consumed under specified conditions in the oxidation of organic and oxidizable inorganic matter in waste water, corrected for the influence of chlorides.

Coliform Group - Group of several types of bacteria which are found in the alimentary tract of warm-blooded animals. The bacteria are often used as an indicator of animal and human fecal contamination of water.

Cone of Depression - The depression, approximately conical in shape, that is formed in a water-table or potentiometric surface when water is removed from an aquifer.

Connate Water - Water that was deposited simultaneously with the geologic formation in which it is contained.

Consumptive Use - That part of the water withdrawn that is no longer available because it has been either evaporated, transpired, incorporated into products and crops, or otherwise removed from the immediate water environment.

Contamination - The degradation of natural water quality as a result of man's activities, to the extent that its usefulness is impaired. There is no implication of any specific limits, since the degree of permissible contamination depends upon the intended end use, or uses, of the water.

Curie - The quantity of any radioactive material giving 3.7×10^{10} disintegrations per second. A picocurie is one trillionth of a curie, or a quantity of radioactive material giving 22.2 disintegrations per minute.

Drainage Well - A well that is installed for the purpose of draining swampy land or disposing of storm water, sewage, or other waste water at or near the land surface.

Dry Well - A borehole or well that does not extend into the zone of saturation.

Effluent - A waste liquid discharge from a manufacturing or treatment process, in its natural state, or partially or completely treated that discharges into the environment.

Eutrophication - The reduction of dissolved oxygen in natural and man-made lakes and estuaries, leading to deterioration of the esthetic and life-supporting qualities.

Evapotranspiration - The combined processes of evaporation and transpiration.

Exfiltration - The leakage of effluent from sewage pipes into the surrounding soils.

Field Capacity - The moisture content of the soil after water has been removed by deep seepage through the force of gravity. It is the moisture retained largely by capillary forces.

Flow Path - The direction of movement of ground water and any contaminants that may be contained therein, as governed principally by the hydraulic gradient.

Fracture - A break in a rock formation due to structural stresses. Fractures may occur as faults, shears, joints, and planes of fracture cleavage.

Ground Water - Water beneath the land surface in the saturated zone that is under atmospheric or artesian pressure. The water that enters wells and issues from springs.

Ground-Water Reservoir - The earth materials and the intervening open spaces that contain ground water.

Hazardous Waste - Any waste or combination of wastes which pose a substantial present or potential hazard to human health or living organisms.

Head - The height above a standard datum of the surface of a column of water that can be supported by the static pressure at a given point.

Heavy Metals - Metallic elements, including the transition series, which include many elements required for plant and animal nutrition in trace concentrations, but which become toxic at higher concentrations. Examples are: mercury, chromium, cadmium, and lead.

Hydraulic Conductivity - The quantity of water that will flow through a unit cross-sectional area of a porous material per unit of time under a hydraulic gradient of 1.00 at a specified temperature.

Hydraulic Fracturing - The fracturing of a rock by pumping fluid under high pressure into a well for the purpose of increasing permeability.

Hydraulic Gradient - The change in static head per unit of distance along a flow path.

Infiltration - The flow of a liquid through pores or small openings.

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Injection Well - A well used for injecting fluids into an underground stratum.

Intermittent Stream - A stream which flows only part of the time.

Ion Exchange - Reversible exchange of ions adsorbed on a mineral or synthetic polymer surface with ions in solution in contact with the surface. In the case of clay minerals, polyvalent ions tend to exchange for nonvalent ions.

Iron Bacteria - Bacteria which can oxidize or reduce iron as part of their metabolic process.

Irrigation Return Flow - Irrigation water which is not consumed in evaporation or plant growth, and which returns to a surface stream or ground-water reservoir.

Leachate - The liquid that has percolated through solid waste or other man-emplaced medium from which soluble components have been removed.

Loading Rate - The rate of application of a material to the land surface.

Mined Ground Water - Water removed from storage when pumpage exceeds ground-water recharge.

Mineralization - Increases in concentration of one or more constituents as the natural result of contact of ground water with geologic formations.

Monitoring (Observation) Well - A well used to measure ground-water levels, and in some cases, to obtain water samples for water-quality analysis.

Nonpoint Source - The contaminant enters the receiving water in an intermittent and/or diffuse manner.

Organic - Being, containing, or relating to carbon compounds, especially in which hydrogen is attached to carbon, whether derived from living organisms or not; usually distinguished from inorganic or mineral.

Overburden - All material (loose soil, sand, gravel, etc.) that lies above bedrock. In mining, any material, consolidated or unconsolidated, that overlies an ore body, especially deposits mined from the surface by open cuts.

Oxidation - A chemical reaction in which there is an increase in valence resulting from a loss of electrons; in contrast to reduction.

Percolate - The water moving by gravity or hydrostatic pressure through interstices of unsaturated rock or soil.

Percolation - Movement of percolate under gravity or hydrostatic pressure.

Perennial Stream - One which flows continuously. Perennial streams are generally fed in part by ground water.

Permeability - A measure of the capacity of a porous medium to transmit fluid.

Piezometric Surface - The surface defined by the levels to which ground water will rise in tightly cased wells that tap an artesian aquifer.

Plume - A body of contaminated ground water originating from a specific source and influenced by such factors as the local ground-water flow pattern, density of contaminant, and character of the aquifer.

Point Source - Any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, or concentrated animal feeding operation from which contaminants are or may be discharged.

Potentiometric Surface - Used synonymously with piezometric surface.

Public Water Supply - A system in which there is a purveyor and customers; the purveyor may be a private company, a municipality, or other governmental agency.

Recharge - The addition of water to the ground-water system by natural or artificial processes.

Reduction - A chemical reaction in which there is a decrease in valence as a result of gaining of electrons.

Runoff - Direct or overland runoff is that portion of rainfall which is not absorbed by soil, evaporated or transpired by plants, but finds its way into streams as surface flow. That portion which is absorbed by soil and later discharged to surface streams is ground-water runoff.

Salaquifer - An aquifer which contains saline water.

Saline - Containing relatively high concentrations of salts.

Salt-Water Intrusion - Movement of salty ground water so that it replaces fresh ground water.

Saturated Zone - The zone in which interconnected interstices are saturated with water under pressure equal to or greater than atmospheric.

Self-Supplied Industrial and Commercial Water Supply - A system from which water is served to consumers free of charge, or from which water is supplied by the operator of the system for his own use.

Sludge - The solid residue resulting from a process or waste-water treatment which also produces a liquid stream (effluent).

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Specific Conductance - The ability of a cubic centimetre of water to conduct electricity; varies directly with the amount of ionized minerals in the water.

Storage (Aquifer) - The volume of water held in the interstices of the rock.

Strata - Beds, layers, or zones of rock.

Subsidence - Surface caving or distortion brought about by collapse of deep mine workings or cavernous carbonate formations, or from overpumping of certain types of aquifers.

Surface Resistivity (Electric Resistivity Surveying) - A geophysical prospecting operation in which the relative values of the earth's electrical resistivity are interpreted to define subsurface geologic and hydrologic conditions.

Surface Water - That portion of water that appears on the land surface, i.e., oceans, lakes, rivers.

Toxicity - The ability of a material to produce injury or disease upon exposure, ingestion, inhalation, or assimilation by a living organism.

Transmissivity - The rate at which water is transmitted through a unit width of an aquifer under a unit hydraulic gradient.

Unsaturated Zone (Zone of Artesian) - Consists of interstices occupied partially by water and partially by air, and is limited above by the land surface and below by the water table.

Upconing - The upward migration of ground water from underlying strata into an aquifer caused by reduced hydrostatic pressure in the aquifer as a result of pumping.

Water Table - That surface in an unconfined ground-water body at which the pressure is atmospheric. It defines the top of the saturated zone.

Water-Table Aquifer - An aquifer containing water under atmospheric conditions.

Well - An artificial excavation that derives fluid from the interstices of the rocks or soils which it penetrates, except that the term is not applied to ditches or tunnels that lead ground water to the surface by gravity. With respect to the method of construction, wells may be divided into dug wells, bored wells, drilled wells, and driven wells.

Well Capacity - The rate at which a well will yield water.

Withdrawal - The volume of water pumped from a well or wells.

APPENDIX C

WORKSHEETS AND ENLARGED NOMOGRAPHS
FOR RAPID ASSESSMENT PROCEDURES

WORKSHEET FOR RAPID ASSESSMENT NOMOGRAPH

ZONE: UNSATURATED _____

SATURATED _____

Site: _____ Date of Incident: _____

Location: _____

On Site Coordinator: _____ Agency: _____

Scientific Support
Coordinator: _____ Agency: _____

Compound Name: _____

Compound Characteristics: _____

REQUIRED PARAMETERS: DATA SOURCES / COMMENTS

C_o = _____   _____

V = _____   _____

D = _____   _____

k = _____   _____

R = $1 + \dfrac{B}{\theta} K_d$ = _____   _____

K_d = _____   _____

B = _____   _____

θ = _____   _____

PRELIMINARY CALCULATIONS:

1. $V^* = V/R$ = _____   3. $k^* = k/R$ = _____

2. $D^* = D/R$ = _____   4. $\sqrt{V^{*2} + 4D^* k^*}$ = _____

5	6	7	8	9				10	11	12
				See Footnote # 2				From Nomograph[3]		
x	t	$x/2D^*$	$\sqrt{4D^* t}$	A_1	A_2	B_1	B_2	M_1	M_2	C/C_o	C

NOMOGRAPH WORKSHEET (con't.)

ZONE: UNSATURATED _____

SATURATED _____

5	6	7	8	9				10		11	12
x	t	$x/2D*$	$\sqrt{4D*t}$	See Footnote # 2				From Nomograph[3]			C
				A_1	A_2	B_1	B_2	M_1	M_2	C/C_0	

Footnotes:

1. Refer to Table 3.1 for definitions and units, and to Chapter 4 for estimation guidelines.

2. A_1 = Col.7 X (Item 1 - Item 4) = $\frac{x}{2D*}$ $(V* - \sqrt{V*^2 + 4D*k*})$

   A_2 = [Col.5 - Col.6 X Item 4] / Col.8 = $\frac{x - t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

   B_1 = Col.7 X (Item 1 + Item 4) = $\frac{x}{2D*}$ $(V* + \sqrt{V*^2 + 4D*k*})$
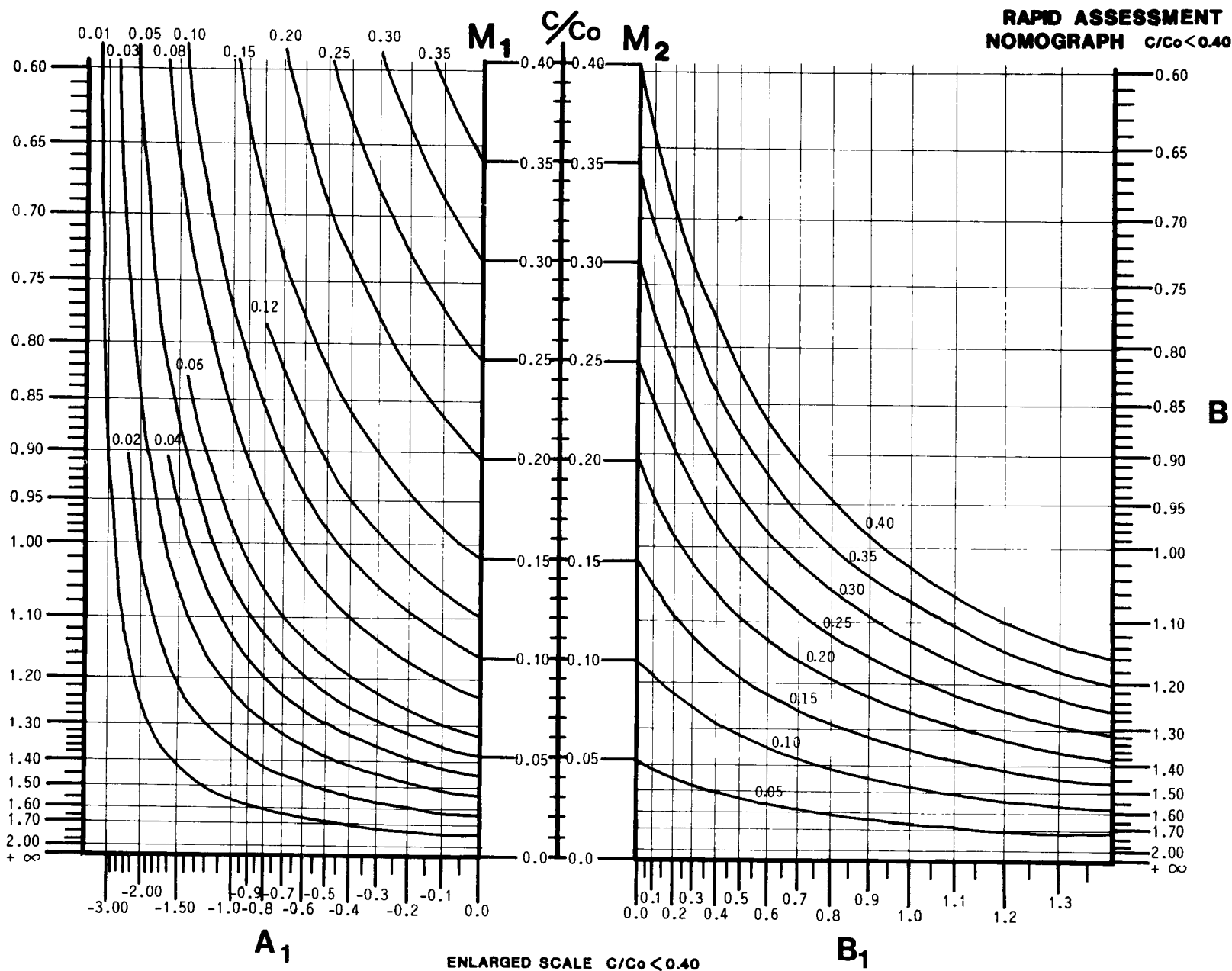
   B_2 = [Col.5 + (Col.6 X Item 4)] / Col.8 = $\frac{x + t\sqrt{V*^2 + 4D*k*}}{\sqrt{4D*t}}$

3. Figure 3.3 or Figure 3.4 (See Figure 3.3 for use of nomograph).

RAPID ASSESSMENT
NOMOGRAPH

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RAPID ASSESSMENT NOMOGRAPH C/Co < 0.40

ENLARGED SCALE C/Co < 0.40

ADDENDUM TO RAPID ASSESSMENT OF POTENTIAL GROUNDWATER CONTAMINATION
UNDER EMERGENCY RESPONSE CONDITIONS

The purpose of this addendum is to provide additional explanation on how to apply the procedures described in this manual to situations involving non-aqueous wastes. In this situation two phase flow may exist and the procedures described in the manual will not yield valid concentration predictions. Two phase flow may exist when both:

$$x < \frac{M}{RC_s A\theta} \quad \text{and} \quad t < \frac{M}{C_s AV\theta}$$

where x = distance

t = time

M = mass of contaminant

C_s = water solubility limit of contaminant

A = area of spill or discharge

V = velocity

R = retardation factor

θ = water fraction of soil

Under these conditions the procedures described in this manual should not be used.

Additionally, the user should understand that C_0 is the initial water phase concentration and can never exceed the water solubility limit. As explained in Section 4.1.2, lacking other information it is recommended that C_0 should be assumed equal to C_s.

Finally, for pulse input problems involving non-aqueous waste, the pulse duration (t_0) should be set equal to $M/(C_s AV\theta)$.

In summary, the following guidelines should be used for non-aqueous wastes:

o Constant Input Problems

    1) set $C_0 = C_s$

    2) apply only where $x > \dfrac{M}{RC_s A\theta}$ and $t > \dfrac{M}{C_s AV\theta}$

o Pulse Input Problems

    1) set $C_0 = C_s$

    2) set $t_0 = M/(C_s AV\theta)$.

    3) apply only where $x > \dfrac{M}{RC_s A\theta}$ and $t > \dfrac{M}{C_s AV\theta}$