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The Multimedia Environmental Pollutant Assessment System (MEPAS)®: Source-Term Release Formulations

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Pacific Northwest Laboratory
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Preface

This report is one of a series of reports that document the mathematical models in the Multimedia Environmental Pollutant Assessment System (MEPAS). Developed by Pacific Northwest National Laboratory[a] for the U.S. Department of Energy, MEPAS is an integrated impact assessment software implementation of physics-based fate and transport models in air, soil, and water media. Outputs are estimates of exposures and health risk assessments for radioactive and hazardous pollutants.

Each of the MEPAS formulation documents covers a major MEPAS component such as source-term, atmospheric, vadose zone/groundwater, surface water, and health exposure/health impact assessment. Other MEPAS documentation reports cover the sensitivity/uncertainty formulations and the database parameter constituent property estimation methods. The pollutant source-term release component is documented in this report.

MEPAS simulates the release of contaminants from a source, transport through the air, groundwater, surface water, or overland pathways, and transfer through food chains and exposure pathways to the exposed individual or population. For human health impacts, risks are computed for carcinogens and hazard quotients for noncarcinogens. MEPAS is implemented on a desktop computer with a user-friendly interface that allows the user to define the problem, input the required data, and execute the appropriate models for both deterministic and probabilistic analyses.

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Summary

The Multimedia Environmental Pollutant Assessment System (MEPAS) is an integrated impact assessment software implementation of physics-based fate and transport models for health and environmental risk assessments for both radioactive and hazardous pollutants. This source-term release component report is one of a series of formulation reports that document the MEPAS mathematical models.

MEPAS is a "multimedia" model; pollutant transport is modeled within, through, and between multiple media (air, soil, groundwater, and surface water). The estimated concentrations in the various media are used to compute exposures and impacts to the environment, to maximum individuals, and to populations.

The MEPAS source-term release component documented in this report includes models for estimating contaminant loss from three different types of source zones (contaminated aquifer, contaminated pond/surface impoundment, and contaminated vadose zone) due to decay/degradation, leaching, wind suspension, water erosion, overland flow, and/or volatilization. When multiple loss processes are assumed to occur simultaneously, the models account for their interaction and calculate an appropriate pollutant mass budget to each loss route. The material in this report is documentation for MEPAS Version 3.2 and the Remedial Action Assessment System (RAAS) Version 1.1.

The ultimate objective of the source-term release component of MEPAS is to calculate a "mass-budgeted" set of contaminant flux versus time functions that describe loss of contaminant from the source zone to a number of different routes. "Mass-budgeted" means that the inventory of each contaminant is apportioned to each loss route in a manner such that the sum of the total calculated contaminant losses to all routes is limited to 100% of the initial inventory. If the user wishes to explicitly enter the contaminant flux to one or more loss routes (based on known or assumed data, or the predictions of some other model), the source-term release component will use the supplied flux versus time function(s) until mass balance considerations dictate that the flux must go to zero (because cumulative contaminant mass loss to all routes has removed 100% of the initial inventory). If the user cannot or does not wish to supply explicit contaminant fluxes to any or all loss routes, the source-term release component contains models that will calculate the flux verses time functions (also according to mass balance considerations). If the user wants to analyze a scenario that assumes contaminant release to only a subset of the possible loss routes for a given type of source zone, loss to undesired routes can be "turned off" by specifying a known flux of zero to those routes.

In all types of contaminant source zones, it is assumed that the contaminants may be present in multiple phases (i.e., in aqueous solution, sorbed to solid particles, in vapor-filled pore space, or in a separate non-aqueous-phase liquid [NAPL] that is immiscible with water and air). The source-term release component contains models to determine which contaminants in the problem scenario will partition into which phases, and to what degree. An important feature of the source-term release component is its ability to calculate aqueous and vapor concentrations of contaminants in equilibrium with a NAPL phase

composed of a changing mixture of contaminants. Different partitioning theory is used when the contaminant is present as a dilute, primary, or intermediate constituent of the NAPL phase.

All types of contaminant source zones are conceptualized as so-called "well-mixed reactors" (i.e., the properties of the zone are assumed spatially uniform throughout). However, for one possible vadose zone condition, this conceptualization leads to unrealistically high estimates of volatilization loss. In this instance, a calculation based on a simple spatial gradient model is used as a bounding calculation for volatilization flux. The contaminant concentrations in the source zone, and in some cases the location of the boundary of the zone, can change over time due to the action of the loss processes.

The source-term release module can be used to simulate "baseline" scenarios as well as scenarios where certain types of remediation methodologies have been implemented at the site. Remediation methodologies that can be simulated for any type of source zone include all methodologies that can be represented merely by changing the magnitude of certain model parameters from their "baseline" values.

For a contaminated aquifer source zone, the contaminant can be present in either the aqueous or sorbed phases, and possibly also an immobile NAPL phase (depending on the inventory). The possible contaminant loss processes considered are first-order decay/degradation within the zone and advective leaching from the zone along with the flowing groundwater.

For a contaminated pond/surface impoundment source zone, the contaminant can be present in either the aqueous or sorbed (to suspended sediment) phases, and possibly also a NAPL phase that exists as small globules suspended throughout the zone (depending on the inventory). The possible contaminant loss processes considered are first-order decay/degradation within the zone, advective leaching from the zone along with the infiltrating water, overland flow from the zone along with runoff water, and volatilization from the pond/surface impoundment surface.

For a contaminated vadose zone source zone, the contaminant can be present in either the aqueous, sorbed, or vapor phases, and possibly also an immobile NAPL phase (depending on the inventory). The possible contaminant loss processes considered are first-order decay/degradation within the zone, advective leaching from the zone along with the percolating vadose zone water, wind suspension of contaminated soil particles from the zone surface, water erosion of contaminated soil particles from the zone surface, and volatilization from the soil surface (possibly through a clean layer of soil above the source zone, which may change thickness over time due to the volatilization process or due to soil particle removal by suspension/erosion). In addition, for this type of source zone, the source-term release component contains models that can calculate loss fluxes from vadose zones subjected to two types of remediation methodologies that require special theory. For these scenarios (i.e., *in situ* vitrification [ISV] and *in situ* solidification [ISS]), the possible contaminant loss processes considered are decay/degradation and leaching.

Theory consists of expressing contaminant loss fluxes through first-order, ordinary differential equations, which are solved in the source-term component by numerical methods (fourth-order Runge-Kutta). This report also presents analytical solutions that are applicable to certain special cases of contaminant release. These analytical solutions can be used to verify the output of the source-term release component in those special cases. Because a numerical solution scheme is used to solve the differential equations of contaminant loss versus time, certain environmental input parameters can be entered as time-varying quantities rather than being constrained to constants. The report ends with a brief summary of the module and its current limitations, and a discussion of plans for further development.

The major outputs from the source-term release component models are sets of contaminant flux versus time pairs (at time intervals equal to the numerical time step) for each contaminant for each selected loss process. These outputs are linked as input to other components as part of the integrated MEPAS exposure and impact evaluation software.

Abbreviations and Acronyms

AET	actual evapotranspiration
COE	U.S. Army Corps of Engineers
EPA	U.S. Environmental Protection Agency
ISS	*in situ* solidification
ISV	*in situ* vitrification
LCD	Local Climatic Data
MEPAS	Multimedia Environmental Pollutant Assessment System
NAPL	non-aqueous-phase liquid
PET	potential evapotranspiration
RAAS	Remedial Action Assessment System
SCS	Soil Conservation Service
USDA	U.S. Department of Agriculture
USLE	universal soil loss equation

Acknowledgments

The development of this multimedia contaminant environmental exposure and risk assessment methodology over the past decade required input from a wide spectrum of engineering and scientific technologies. The original MEPAS concept was developed by G. Whelan and B. L. Steelman. They were joined by J. G. Droppo, J. W. Buck, K. A. Higley, D. L. Strenge, and B. L. Hoopes to form the initial MEPAS development team.

Many of the models now implemented in the source-term release component are based on models that were originally implemented in air, groundwater, and surface water components of previous versions of MEPAS. This is especially true of the models used to calculate selected parameters that appear in contaminant mass loss equations, many of which have been implemented here without further modification. Therefore, this source-term development effort is indebted to staff who had previously selected, derived, or programmed theory related to water balance, wind suspension, water erosion, and volatilization. Portions of the documentation of theory used to calculate selected parameters that appear in contaminant mass loss equations, which has appeared in formulations documents for previous versions of MEPAS, have been included in this report. Several staff responsible for this documentation (i.e., G. Whelan, J. P. McDonald, J. G. Droppo, and J. W. Buck) have therefore been included as authors on this report. However, in addition to staff included as authors, these efforts have included Karl Castleton and Steve Hwang.

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1.0 Introduction

The Multimedia Environmental Pollutant Assessment System (MEPAS) is a physics-based tool for simulating contaminant source release, environmental transport and transformation, human exposure and dose, and risk in a multimedia environmental system. In the environmental scenarios that MEPAS can address, contamination can move through the environment along several different transport pathways (i.e., vadose zone/groundwater pathway, overland flow/surface water pathway, and atmospheric pathway). MEPAS consists of a collection of linked computer modules (i.e., computer codes for simulating one or more of the aforementioned processes) controlled by a user-friendly interface. The material in this report is documentation for the MEPAS Version 3.2 and the Remedial Action Assessment System (RAAS) Version 1.1.

The MEPAS source-term release module documented in this report includes models for estimating contaminant loss from three different types of source zones: contaminated aquifer, contaminated pond/surface impoundment, and contaminated vadose zone. In all types of contaminant source zones, it is assumed that the contaminants may be present in multiple phases (i.e., in aqueous solution, sorbed to solid particles, in vapor-filled pore space, or in a separate non-aqueous-phase liquid [NAPL] that is immiscible with water and air). The source-term release module contains models to determine which contaminants in the problem scenario will partition into which phases, and to what degree. Depending on the type of source zone, it is assumed that the processes causing contaminant release from the source zone to an environmental transport pathway could be leaching (groundwater pathway), wind suspension (atmospheric pathway), water erosion (overland/surface water pathway), overland flow (overland/surface water pathway), and/or volatilization (atmospheric pathway). In addition, contaminants could be lost from the source zone by radioactive decay or degradation within the zone.

The source-term release module contains models for simulating "baseline" (i.e., unremediated) scenarios for all three types of source zones. These same models can be used to simulate remediated sites (for all three types of source zones) if the remediation methodology can be represented merely by changing the magnitude of certain model parameters from their "baseline" values. In addition, for the vadose zone source zone, the source-term release module contains models that can calculate loss fluxes from vadose zones subjected to two types of remediation methodologies that require special theory: *in situ* vitrification (ISV) and *in situ* solidification (ISS).

The ultimate objective of the source-term release component of MEPAS is to calculate a "mass-budgeted" set of contaminant flux versus time functions that describe the simultaneous loss of contaminants from the source zone to a number of different routes. When multiple loss processes are assumed to occur simultaneously, the mathematical models implemented in the source-term release module account for their synergistic or antagonistic interaction. "Mass-budgeted" means that the inventory of each contaminant is apportioned to each loss route (by the implemented physics-based theory) in a manner such that the sum of the calculated contaminant losses to all routes is limited to 100% of the initial inventory.

The source-term release module has been developed to allow the user flexibility in how the contaminant release to different routes is simulated. If the user wishes to explicitly enter the contaminant flux to one or more loss routes (based on known or assumed data, or the predictions of some other model), the source-term release component will use the supplied flux versus time function(s) until mass balance considerations dictate that the flux must go to zero (because cumulative contaminant mass loss to all routes has removed 100% of the initial inventory). If the user cannot or does not wish to supply explicit contaminant fluxes to any or all loss routes, the source-term release component contains models that will calculate the flux verses time functions (also according to mass balance considerations). If the user wants to analyze a scenario that assumes contaminant release to only a subset of the possible loss routes for a given type of source zone, loss to undesired routes can be "turned off" by specifying a known flux of zero to those routes.

Section 2.0 of this report describes some basic attributes of the source-term release module that are applicable to any of the three types of contaminant source zones simulated by it. These include discussions of contaminant phase partitioning theory and the general mathematical approach to describing contaminant mass loss rates.

Sections 3.0, 4.0, and 5.0 give details of the specific approaches for addressing contaminated aquifer, pond/surface impoundment, and vadose zone source zones, respectively. Each of these sections contains a description of: the conceptual model assumed for that source zone, the mathematical models that lead to the contaminant flux expressions (if the user allows MEPAS to compute the release functions), the numerical solution procedure that produces a set of "mass-budgeted" release fluxes for each contaminant, analytical solutions for certain special cases (i.e., simplified scenarios) that could be used to verify the source-term release module outputs, methods already implemented in the module for calculating certain parameters in the contaminant flux expressions, and how to use user-supplied flux versus time functions for one or more loss routes (if the user does not want MEPAS to compute the release functions). The theory presented for the contaminated aquifer and pond/surface impoundment source zones is relatively straightforward because no synergistic or antagonistic interactions between loss processes occur, and because the source zone dimensions remain constant. On the other hand, the theory presented for the contaminated vadose zone source zone is relatively complex because interactions between loss processes do occur, and because the loss processes may cause the dimensions of the source zone to change in several ways. Furthermore, auxiliary theory implemented in the module to calculate selected parameters used in the vadose zone mass loss equations is relatively extensive.

Section 6.0 contains a brief summary of the module and its current limitations, and a discussion of plans for further development. Section 7.0 is a list of all symbols used in this report, along with their definitions and their associated units. Section 8.0 lists all references cited in the report. Finally, a complete listing of all the input parameters required by the source-term release module, along with the necessary units, is given in Appendix A.

2.0 General Contaminant Phase Partitioning and Loss Rate Theory

This section describes some basic attributes of the source-term release module that are applicable to any of the three types of contaminant source zones addressed by it. Firstly, it discusses the different kinds of contaminants that can be included in problem scenarios, and how the source-term release module obtains certain basic physicochemical properties (for each contaminant) that it needs for its calculations. Secondly, it discusses the overall phase partitioning theory implemented in the module. Thirdly, it discusses the general mathematical form of the expressions used for contaminant mass loss flux rate.

2.1 Contaminants

As is the case for MEPAS in general, the source-term release module can accommodate source zones containing both radioactive and hazardous chemical pollutants. The hazardous chemicals can be either organic or inorganic compounds. MEPAS and RAAS, through their user interfaces, have the ability to access databases of physicochemical and exposure-related properties for a wide variety of contaminants. These databases are augmentations of the database described by Strenge and Peterson (1989), which was originally developed for an earlier version of MEPAS. The RAAS contaminant database currently contains 409 contaminants categorized into 14 different classes. Currently, when using RAAS Version 1.1, source-term release calculations can only be performed for contaminants that are in the database. However, when using MEPAS Version 3.2, source-term release calculations can be performed for contaminants currently in the MEPAS database, plus any contaminants for which the user can supply the required physical and chemical input parameters.

The source-term release module requires certain contaminant-specific properties (e.g., aqueous solubility, saturated vapor pressure, Henry's Law constant, inorganic or nuclide sorption coefficient, organic carbon partition coefficient, octanol-water partition coefficient, decay/degradation half life, diffusion coefficient in air, and effective diffusion coefficient in grout) as input parameters if loss fluxes are to be calculated by the models implemented in the module. Exactly which of these properties are required for a given run depends on the contaminant as well as the type of contaminant source zone being analyzed and the types of release pathways being considered. The source-term release module and the contaminant property databases have been developed in unison so that the mathematical models implemented in the module use the kind of contaminant information available in the databases. When a contaminant is chosen for inclusion in the analyses, default values for all of the relevant contaminant-specific properties are automatically selected for input parameters. However, the user also has the option of changing the values of some of these parameters if there are more appropriate data available for the specific scenario under analysis. (These contaminant property input parameters are included in the Appendix A listing.)

Half lives for radionuclides are single-valued and well known. Values of first-order decay half lives and first-order decay rate coefficients for radionuclides are present in the databases. Many contaminants other than radionuclides can also be transformed into other compounds in real-world environments (e.g., organic chemicals undergoing biodegradation). However, the degradation process does not necessarily follow first-order kinetics; nor does it necessarily have a unique half life. Describing the process with a first-order equation involves defining an "effective" first-order decay coefficient or half life that could vary with the microbial population size, the redox potential of the environment, and the concentrations of other substances needed by the microbes (e.g., carbon sources, nutrients, and electron acceptors). The MEPAS contaminant property database assumes that first-order decay coefficients for nonradionuclides are zero. On the other hand, the RAAS database contains degradation half life values applicable to biodegradation in a "reference" environment. However, if users have a specific value for the half life that they wish to use, they can override the default values in the databases.

2.2 Phase Partitioning Theory

The source-term release module treats contaminants differently with respect to phase partitioning calculations. The module determines whether a NAPL phase exists, and then uses one of two kinds of phase partitioning theory (depending on the NAPL phase existence and the contaminant.)

2.2.1 Allowable Contaminants in Phases Present

In general, the source-term release module assumes that a contaminant may be present in the source zone in multiple phases (i.e., in aqueous solution, sorbed to solid particles, in vapor-filled pore space, or in a separate NAPL that is immiscible with water and air). However, not every phase is present in each type of contaminant source zone. For example, a contaminated aquifer or contaminated pond/surface impoundment source zone has no vapor phase, a contaminated pond/surface impoundment source zone may not have a solid-sorbent phase, and any type of source zone may not have a NAPL phase. Furthermore, the source-term release module does not allow all contaminants to partition into every phase that is present. This is reasonable because even though, in a strict thermodynamic sense, every contaminant should have a nonzero aqueous solubility, NAPL solubility, saturated vapor pressure, and solid surface partition coefficient, there are practical limits on the phase partitioning behavior of different contaminants in real-world systems.

The source-term release module assumes that all contaminants can partition into an aqueous, solid-sorbent, or vapor phase (if a solid-sorbent or vapor phase is present in the source zone). However, this does not mean that all contaminants will actually be present in the solid-sorbent or vapor phase. Some of the contaminants in the chemical property database have values of zero for the sorption coefficient, or for some other chemical property that is used to estimate the sorption coefficient. This means that solid-sorbent terms in the phase partitioning equations will be calculated to be identically equal to zero. In addition, most radionuclides and inorganic contaminants have negligibly small saturated vapor pressures and Henry's Law constants. To reflect this, the chemical property database contains values of zero for these properties for some of them. There are also organic contaminants in the database with low values of saturated vapor pressure and Henry's Law constant. Therefore, even though a vapor-phase term is always included in the partitioning theory, it can be identically zero or negligibly small (i.e., computationally equal to zero) if the contaminant's properties cause it to be.

On the other hand, the source-term release module does not assume that all contaminants can partition into a NAPL phase (if one is present in the source zone). A reasonably good conceptualization of the NAPL phase would be to assume that it is composed of all organic contaminants in the source zone, and that it contains none of the radionuclides or inorganic contaminants in the source zone. However, the source-term release module (associated with RAAS Version 1.1) is not currently tied into the RAAS contaminant classification scheme. Therefore it cannot explicitly identify whether a contaminant is an organic compound. However, organic contaminants in the database tend to have higher values for the Henry's Law constant than radionuclides or inorganic contaminants. So, the source-term release module currently uses a contaminant's Henry's Law constant as a quantitative metric (i.e., contaminants with modified Henry's Law constants [dimensionless form] greater than or equal to 10^{-7} are assumed to partition into the NAPL phase).

2.2.2 NAPL Phase Existence Determination

There are two basic kinds of partitioning theory implemented in the source-term release module, depending on whether a NAPL phase exists. When no NAPL phase is present, the theory required to describe the phase partitioning behavior is much simpler. Because the contaminant loss flux equations implemented in the module require a numerical solution procedure, contaminant masses and loss fluxes are calculated at discrete time intervals. At the beginning of each time step, the module determines if a NAPL phase must exist based on the source zone properties and the contaminant inventories in the source zone at that time. After this determination, the appropriate type of phase partitioning theory is used for the calculations associated with that time step.

The test criterion for the existence of a NAPL phase was developed as follows. For a given source zone (i.e., for a source zone with a given volumetric water content, volumetric air content, bulk density of solid-sorbent, and overall volume), there is a maximum upper limit to the amount of contaminant that can be accommodated in the aqueous, solid-sorbent, and vapor phases. This limit depends on the contaminant's aqueous solubility, saturated vapor pressure (or saturated vapor concentration), and sorption coefficient. Therefore, summing up the maximum amounts of contaminant that can be accommodated in each of these three phases, and comparing this to the actual contaminant mass (or activity) in the source zone is a way to determine whether a NAPL phase must exist. A general way to express this criterion in mathematical terms is

$$M_i - (\theta_w C_{wi}^{sol} + \theta_a C_{vi}^{sat} + \beta K_{di} C_{wi}^{sol}) \cdot V > 0 \tag{2.1}$$

where M_i is the total mass or activity of contaminant *i* in the source zone (g or Ci)
θ_w is the volumetric water content of the soil (unitless)
C_{wi}^{sol} is the aqueous solubility of contaminant *i* (g cm^{-3} or Ci cm^{-3})
θ_a is the volumetric air content of the soil (unitless)
C_{vi}^{sat} is the saturated vapor concentration of contaminant *i* (g cm^{-3} or Ci cm^{-3})
β is the bulk density of the solid-sorbent phase (g cm^{-3});

K_{di} is the linear equilibrium sorption coefficient for contaminant *i* to a solid sorbent ($cm^3\ g^{-1}$)
V is the overall volume of the contaminated source zone (cm^3).

[All symbols used in this report are defined in Section 7.0.] This expression (and all subsequent phase partitioning theory) is commensurate with the conceptualization that the source zone is a "well-mixed reactor" (i.e., its properties are spatially uniform throughout).

A criterion equivalent to the one in Equation 2.1 is checked for each contaminant that could be part of a NAPL phase (i.e., all contaminants with Henry's Law constants > 10^{-7}). If it is untrue for all of them, the source-term release module assumes that a NAPL phase does not exist. If it is true for one or more of them, the source-term release module assumes that a NAPL phase exists (and that all of these contaminants will partition into the NAPL phase to some degree). The exact mathematical form of the criterion that is actually checked in the source-term release module calculations varies depending on the type of contaminant source zone under analysis (i.e., how the volume of the source zone, V, is explicitly described in terms of other source zone parameters). These exact forms are presented in the report sections dedicated to the three different source zones (Sections 3.0, 4.0, and 5.0).

2.2.3 Partitioning Theory When No NAPL Phase Exists

If no NAPL phase exists, the phase partitioning theory for any individual contaminant is independent of the other contaminants. In this case, an overall total contaminant concentration in the source is defined using the total contaminant mass (or activity) present in the source zone and the overall volume of the source zone:

$$C_{Ti} = \frac{M_i}{V} \tag{2.2}$$

where C_{ti} is the overall total concentration of contaminant *i* in a bulk volume of source zone ($g\ cm^{-3}$ or $Ci\ cm^{-3}$).

This overall total concentration can be related to the amounts in each phase by

$$C_{Ti} = \theta_w C_{wi} + \theta_a C_{vi} + \beta C_{si} \tag{2.3}$$

where C_{wi} is the concentration of contaminant *i* in the aqueous phase ($g\ cm^{-3}$ or $Ci\ cm^{-3}$)
C_{vi} is the concentration of contaminant *i* in the vapor phase ($g\ cm^{-3}$ or $Ci\ cm^{-3}$)
C_{si} is the concentration of contaminant *i* in the sorbed phase ($g\ g^{-1}$ or $Ci\ g^{-1}$).

If we assume that Henry's Law is valid for aqueous-vapor partitioning, and that the aqueous-sorbed partitioning is governed by linear equilibrium sorption, Equation 2.3 can be rewritten as

$$C_{Ti} = (\theta_w + \theta_a K_{Hi} + \beta K_{di}) C_{wi} = \frac{(\theta_w + \theta_a K_{Hi} + \beta K_{di})}{K_{Hi}} C_{vi} \tag{2.4}$$

where K_{Hi} is the modified Henry's Law constant for contaminant *i* (concen./concen. basis) for partitioning between aqueous solution and vapor (unitless).

If we define a parameter, R_i, to be

$$R_i = 1 + \left(\frac{\theta_a K_{Hi} + \beta K_{di}}{\theta_w} \right) \tag{2.5}$$

Equation 2.4 can be simplified to

$$C_{Ti} = \theta_w R_i C_{wi} = \frac{\theta_w R_i}{K_{Hi}} C_{vi} \tag{2.6}$$

where R_i is the retardation factor, or phase apportionment factor, for contaminant *i* (unitless).

For the contaminated vadose zone and contaminated aquifer source zones, the parameter R_i can be identified as the commonly reported retardation factor.(a) For the contaminated pond/surface impoundment source zone, the parameter R_i is more appropriately identified as a phase apportionment factor.(b)

The source-term release module needs values of the aqueous and vapor concentrations of the contaminants for the mass loss flux calculations. Combining Equations 2.2 and 2.6, these concentrations can be expressed as

$$C_{wi} = \frac{M_i}{\theta_w R_i V} \tag{2.7}$$

$$C_{vi} = \frac{K_{Hi} M_i}{\theta_w R_i V} \tag{2.8}$$

Note that, because of the way NAPL phase nonexistence was determined (Equation 2.1), Equations 2.7 and 2.8 may result in an aqueous or vapor concentration that exceeds the contaminant's aqueous solubility or saturated vapor concentration. It is possible for the aqueous concentration calculated by Equation 2.7 to be greater than the aqueous solubility if the value of the Henry's Law constant for the contaminant *is less than* the ratio of its saturated vapor concentration and its aqueous solubility (and if the total contaminant mass is near the saturation limit). Conversely, it is possible for the vapor concentration calculated by

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(a) In these scenarios, β is more explicitly defined as β_s, the soil bulk density. In addition, for a contaminated aquifer, the volumetric air content, θ_a, is zero, and the volumetric water content, θ_w, is more explicitly defined as the total porosity, θ_t.

(b) In this scenario, β is more explicitly defined as β_{ss}, the suspended sediment concentration.

Equation 2.8 to be greater than the saturated vapor concentration if the value of the Henry's Law constant for the contaminant *is greater than* the ratio of its saturated vapor concentration and its aqueous solubility (and if the total contaminant mass is near the saturation limit). What this means is that Henry's Law is not really valid for concentrations all the way up to the saturation limit. However, the source-term release module considers that Henry's Law is still valid over the entire concentration range, and merely limits the aqueous or vapor concentration to its saturated value when Equation 2.7 or 2.8 would predict an unrealistically high value.

Equations 2.7 and 2.8 are only general forms of the equations used by the module. The exact mathematical forms of the equations actually used in the calculations vary depending on the type of contaminant source zone under analysis (i.e., how the volume of the source zone, V, is explicitly described in terms of other source zone parameters). These exact forms are presented in the report sections dedicated to the three different source zones (Sections 3.0, 4.0, and 5.0).

2.2.4 Partitioning Theory When a NAPL Phase Exists

If a NAPL phase exists, two kinds of phase partitioning theory are used. All contaminants that are not part of the NAPL phase (i.e., all contaminants with Henry's Law constants $\leq 10^{-7}$) are assumed to behave independently of one another, and are assumed to partition between aqueous, solid-sorbent, and vapor phases according to the theory presented in Section 2.2.3. The partitioning behaviors of all contaminants that are part of the NAPL phase (i.e., Henry's Law constants $> 10^{-7}$) are interdependent because the aqueous and vapor concentrations of each of these contaminants is controlled by the composition of the NAPL phase (which depends on all contaminants).

An exact phase partitioning calculation (for the contaminants that can be a part of the NAPL phase) would require a simultaneous calculation of volumetric fluid contents (for water, air, and NAPL), and contaminant concentrations in all phases. This type of full phase distribution model would require a complex and iterative algorithm (which could take a significant amount of time to run for each time step). The current version of the source-term release module does not contain such a model; but, rather, makes the simplifying assumption that the composition of the NAPL phase is the same as it would be if all of the contaminant mass was in the NAPL phase. It then further assumes that the volumetric water and air contents are equal to what they would be if there was no NAPL phase present.

For all contaminants that can be part of the NAPL phase, the source-term release module first calculates mole fractions and concentrations in the NAPL phase for each contaminant. NAPL-phase mole fractions are calculated by

$$X_{oi} = \frac{\left(\dfrac{M_i}{M_{mi}}\right)}{\displaystyle\sum_{i=1}^{n_{cn}} \left(\dfrac{M_i}{M_{mi}}\right)} \qquad (2.9)$$

where X_{oi} is the mole fraction of contaminant *i* in the NAPL phase (unitless)
M_{mi} is the molecular weight of contaminant *i* (g mol^{-1})
n_{cn} is the total number of constituents in the NAPL phase (unitless)
i is the index on contaminant (unitless).

The NAPL-phase concentrations are calculated by

$$C_{oi} = \frac{M_i}{\sum_{i=1}^{n_{cn}} \left(\frac{M_i}{\rho_{li}} \right)} \tag{2.10}$$

where C_{oi} is the concentration of contaminant *i* in the NAPL phase (g cm^{-3} or Ci cm^{-3})
ρ_{li} is the density of contaminant *i* in the pure liquid form (g cm^{-3}).

Note that Equation 2.10 implicitly assumes that "volume-of-mixing" effects are negligible (i.e., when different liquids mix, the total mixed volume is equal to the sum of the individual separate volumes).

For partitioning equilibrium between the NAPL and vapor phases, the module assumes that an analogue of the modified (i.e., dimensionless) Henry's Law is valid when the contaminant is present as a dilute constituent of the NAPL phase (i.e., when its concentration is sufficiently close to 0):

$$C_{vi} = K_{Hi}^{org} C_{oi} \tag{2.11}$$

where K_{Hi}^{org} is the modified "Henry's Law" constant for contaminant *i* (concen./concen. basis) for partitioning between NAPL and vapor (unitless).

Note that the superscript "org" is used on the dimensionless Henry's constant to highlight the fact that this should be the value for partitioning from an organic liquid phase rather than from an aqueous phase (which is the usual value reported for Henry's Law constants). This value, of course, depends on the exact composition of the organic liquid phase. However, as a first approximation, this parameter can be estimated by

$$K_{Hi}^{org} \approx \frac{K_{Hi}}{K_{owi}} \tag{2.12}$$

where K_{owi} is the octanol-water partition coefficient for contaminant *i* (unitless).

The module assumes that Raoult's Law is valid when the contaminant is present as a primary constituent of the NAPL phase (i.e., when its mole fraction is sufficiently close to 1):

$$C_{vi} = C_{vi}^{sat} X_{oi} \tag{2.13}$$

Figure 2.1 illustrates these "Henry's Law" and Raoult's Law type of relationships between vapor concentration and NAPL composition via the linear segments drawn below some low cutoff value and above some high cutoff value of NAPL-phase mole fraction. For intermediate mole fractions, the vapor concentration will be somewhere in between the values at the cutoff mole fractions. The source-term release module assumes that the vapor concentration in equilibrium with a NAPL phase containing the contaminant at an intermediate mole fraction can be calculated as a linear interpolation between the two values at the extremes of the "Henry's Law" and Raoult's Law regimes (as illustrated in Figure 2.1). For partitioning equilibrium between the NAPL and aqueous phases, the module again assumes that an analogue of the modified (i.e., dimensionless) Henry's Law is valid when the contaminant is present as a dilute constituent of the NAPL phase (i.e., when its concentration is sufficiently close to 0):

$$C_{wi} = K_{wi}^{org} C_{oi} \tag{2.14}$$

where K_{wi}^{org} is the analogue of the modified "Henry's Law" constant for contaminant *i* for partitioning between NAPL and aqueous phases (unitless).

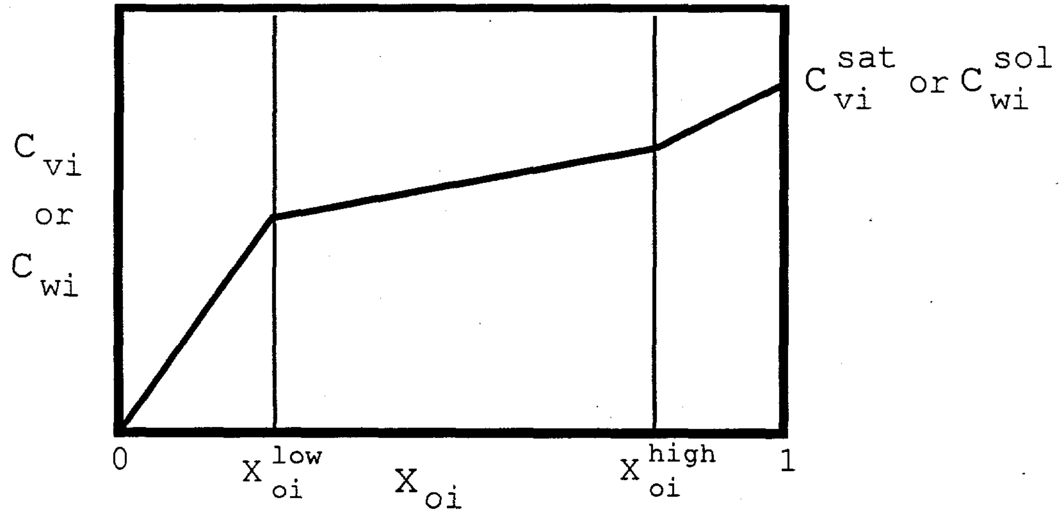

Figure 2.1. Approximate Representation of Contaminant Vapor or Aqueous Concentration as a Function of NAPL-Phase Mole Fraction. The region below X_{oi}^{low} is in the "Henry's Law" regime; and the region above X_{oi}^{high} is in the "Raoult's Law" regime.

The value of K_{wi}^{org}, of course, depends on the exact composition of the organic liquid phase. However, as a first approximation, this parameter can be estimated by

$$K_{wi}^{org} \approx \frac{1}{K_{owi}} \tag{2.15}$$

The module also assumes that an analogue of Raoult's Law is valid (i.e., ideal solution behavior) when the contaminant is present as a primary constituent of the NAPL phase (i.e., when its mole fraction is sufficiently close to 1):

$$C_{wi} = C_{wi}^{sol} X_{oi} \tag{2.16}$$

Because of the similarity between how the source-term release module conceptualizes equilibrium partitioning between a NAPL phase and a vapor or aqueous phase, Figure 2.1 also illustrates the "Henry's Law", "Raoult's Law", and intermediate region type of relationships used to calculate aqueous concentration from NAPL composition.

Given the general forms of the phase equilibria curves in Figure 2.1, the NAPL-phase mole fractions at which the partitioning theory transitions from one regime to another must still be determined. The source-term release module assumes that the high and low cutoff values of X_{oi} are chosen such that the ranges of mole fraction in which "Henry's Law" and "Raoult's Law" relationships are applicable are equal in length (i.e., $X_{oi}^{low} - 0 = 1 - X_{oi}^{high}$). They are also chosen such that the intermediate line is either strictly horizontal or strictly vertical (which depends on the relative magnitude of K_{Hi}^{org} or K_{wi}^{org}). This means that the module assumes that the actual C_{vi} or C_{wi} versus X_{oi} curve looks like the curve in either Figure 2.2 or Figure 2.3.

Determining transition mole fractions that give equally wide regions for the two limiting law regimes is accomplished by determining the mole fraction at which

$$K_{Hi}^{org} C_{oi}^{transv} = C_{vi}^{sat} \left(1 - X_{oi}^{transv}\right) \tag{2.17}$$

for the NAPL/vapor equilibrium, and at which

$$K_{wi}^{org} C_{oi}^{transw} = C_{wi}^{sol} \left(1 - X_{oi}^{transw}\right) \tag{2.18}$$

for the NAPL/aqueous equilibrium.[a] Note that the "Henry's Law" types of relationships (Equations 2.17 and 2.18) are written in terms of NAPL-phase concentrations rather than mole fractions. Therefore, before the transition mole fractions can be calculated, the concentration variables must be converted to mole fractions. This conversion relationship is given by

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(a) Note that in Equations 2.17 and 2.18, the variables with 'trans•' in their superscript represent the low transition mole fractions or concentrations. The high transition mole fractions are equal to one minus those values because of the assumption of equally wide regions.

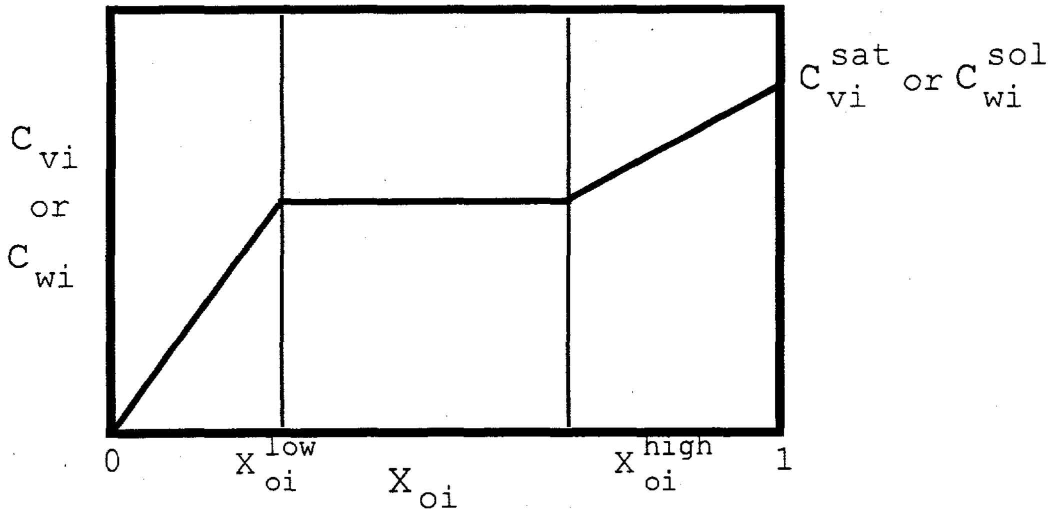

Figure 2.2. Representation of Equilibrium Contaminant Partitioning Between NAPL and Vapor or Aqueous Concentration as a Function of NAPL-Phase Mole Fraction: Implementation for the High K_{Hi}^{org} or K_{wi}^{org} Case.

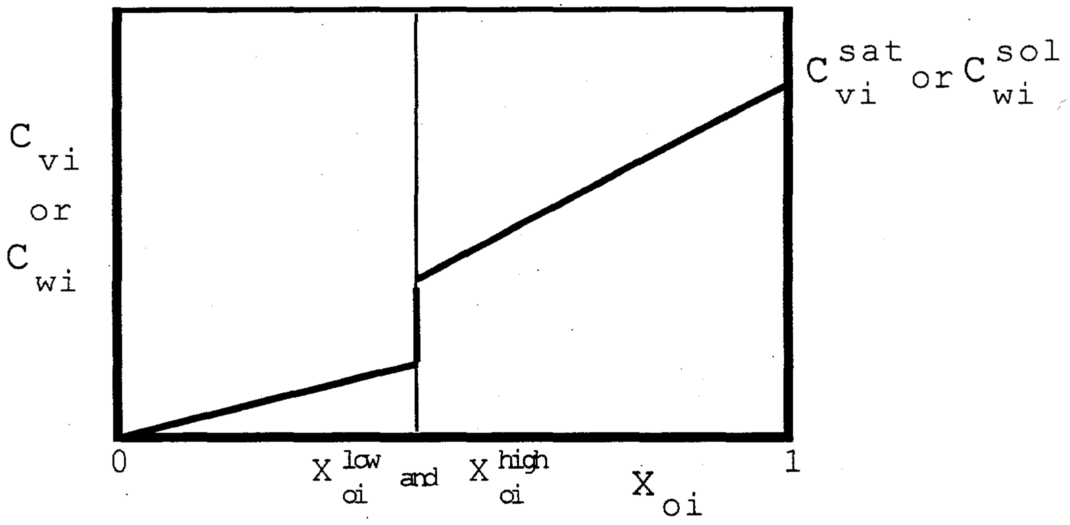

Figure 2.3. Representation of Equilibrium Contaminant Partitioning Between NAPL and Vapor or Aqueous Concentration as a Function of NAPL-Phase Mole Fraction: Implementation for the Low K_{Hi}^{org} or K_{wi}^{org} Case.

$$C_{oi} = \left[\frac{1}{\rho_{li}} + \frac{\sum\limits_{\substack{k=1 \\ k \neq i}}^{n_{cn}} \left(\frac{M_k}{\rho_{lk}} \right)}{M_{mi} \sum\limits_{\substack{k=1 \\ k \neq i}}^{n_{cn}} \left(\frac{M_k}{M_{mk}} \right)} \left(\frac{1 - X_{oi}}{X_{oi}} \right) \right]^{-1} \tag{2.19}$$

where k is the index on the contaminants other than contaminant *i* (unitless).

Using Equation 2.19 to convert the concentration variables in Equations 2.17 and 2.18, and then moving everything to the left-hand sides of the equations, these two equations become

$$K_{Hi}^{org} \left[\frac{1}{\rho_{li}} + \frac{\sum\limits_{\substack{k=1 \\ k \neq i}}^{n_{cn}} \left(\frac{M_k}{\rho_{lk}} \right)}{M_{mi} \sum\limits_{\substack{k=1 \\ k \neq i}}^{n_{cn}} \left(\frac{M_k}{M_{mk}} \right)} \left(\frac{1 - X_{oi}^{transv}}{X_{oi}^{transv}} \right) \right]^{-1} - C_{vi}^{sat} \left(1 - X_{oi}^{transv} \right) = 0 \tag{2.20}$$

$$K_{wi}^{org} \left[\frac{1}{\rho_{li}} + \frac{\sum\limits_{\substack{k=1 \\ k \neq i}}^{n_{cn}} \left(\frac{M_k}{\rho_{lk}} \right)}{M_{mi} \sum\limits_{\substack{k=1 \\ k \neq i}}^{n_{cn}} \left(\frac{M_k}{M_{mk}} \right)} \left(\frac{1 - X_{oi}^{transw}}{X_{oi}^{transw}} \right) \right]^{-1} - C_{wi}^{sol} \left(1 - X_{oi}^{transw} \right) = 0 \tag{2.21}$$

The source-term release module then uses a modified Newton-Raphson root-finding algorithm (Press et al. 1988) to solve Equations 2.20 and 2.21 for their respective lower transition mole fractions. Once these lower transition mole fractions are determined, they are compared to 0.5. If the lower transition mole fraction is ≤ 0.5, a phase equilibrium curve shape like the one in Figure 2.2 is assumed. If the lower transition mole fraction is > 0.5, it is reset identically equal to 0.5 and a phase equilibrium curve shape like the one in Figure 2.3 is assumed.

As stated in Section 2.2.3, the source-term release module ultimately needs values of the aqueous and vapor concentrations of the contaminants for the mass loss flux calculations. When a NAPL phase is present, these are calculated as follows. The contaminant's mole fraction in the NAPL phase is compared to the transition mole fractions (for vapor and aqueous equilibria) that have been previously calculated by the aforementioned method. This determines which region of the phase equilibria curves (Figure 2.2 or 2.3) the contaminant falls into. Based on that determination, the vapor concentration is calculated by using either Equation 2.11 or 2.13, or by setting it equal to the value at the transition mole fractions (if the actual mole fraction is in the intermediate region of a curve like that in Figure 2.2). Similarly, the aqueous concentration is calculated by using either Equation 2.14 or 2.16, or by setting it equal to the value at the transition mole fractions (if the actual mole fraction is in the intermediate region of a curve like that in Figure 2.2).

2.3 General Form of Contaminant Loss Rate Expressions

In general, the mass (or activity) of contaminant *i* in the source zone decreases over time because the contaminant is being removed from the zone by a number of different processes. The processes considered by the source-term release module are first-order decay/degradation, leaching to the vadose zone or groundwater, wind suspension of contaminated surface soil particles, water erosion of contaminated surface soil particles, overland flow of contaminated water from the source, and volatilization from the source into the atmosphere. The overall rate of change of contaminant mass in the source zone can be related to the mass loss rates (i.e., mass fluxes) to each loss route by the following general differential equation:

$$\frac{dM_i}{dt} = \left[\frac{dM_i}{dt}\right]_{decay} + \left[\frac{dM_i}{dt}\right]_{leach} + \left[\frac{dM_i}{dt}\right]_{susp} + \left[\frac{dM_i}{dt}\right]_{eros} + \left[\frac{dM_i}{dt}\right]_{over} + \left[\frac{dM_i}{dt}\right]_{vol} \tag{2.22}$$

where t is the time since initial condition of the source zone. (yr)

For each type of contaminated source zone, each mass flux term on the right-hand side of Equation 2.22 must either be set identically to zero (if that particular loss process does not apply to that type of source zone) or defined by appropriate theoretical expressions derived from the physics and chemistry of the loss processes. When multiple processes occur simultaneously, they can interact. This synergistic or antagonistic process interaction can cause the mathematical expression for a given term in Equation 2.22 to be different from what it would be if that process was the only one removing mass from the source zone. The explicit forms of these terms are derived in the report sections related to each type of source zone (Sections 3.0, 4.0, and 5.0).

Once the right-hand side of Equation 2.22 is expressed as a function of contaminant mass and time, the resulting first-order, ordinary differential equation can be solved by standard numerical methods to update the contaminant mass at discrete time intervals. (Note that for the contaminated vadose zone source zone, an additional differential equation must be solved simultaneously.) The individual terms on the right-hand side of Equation 2.22 (which can also be expressed as first-order, ordinary differential equations) are solved numerically as part of the overall numerical solution of Equation 2.22. The results of the calculations for the individual terms are used to produce the mass loss fluxes to each loss route at discrete time intervals. Because the behavior of some contaminants is linked with that of other contaminants (i.e., those present in a NAPL phase), the masses and loss fluxes of all contaminants are updated within a single time step before the module proceeds to calculations for the next time step.

3.0 Contaminated Aquifer

Consider that the contaminated source zone is located below the water table in a groundwater aquifer. The source-term release module conceptualizes this zone to be a rectangular parallelopiped with volume V that has length L_x in the horizontal direction parallel to the average groundwater flow, width L_y in the horizontal direction perpendicular to the average groundwater flow, and height L_z in the vertical direction.

The source zone contains an aqueous phase (the groundwater), a solid-sorbent phase (the porous aquifer matrix), and may contain a NAPL phase (if the masses of any of the contaminants that may partition into a NAPL phase are above the saturation limits of the other two phases). Because the source zone is below the water table there is no vapor phase. The source zone is assumed to be a so-called "well-mixed reactor," which means that its properties are assumed to be spatially uniform throughout.

Section 2.2.2 describes how the source-term release module tests to determine if a NAPL phase exists (based on the current masses of contaminants in the source zone) at the beginning of each time step. Equation 2.1 in Section 2.2.2 is the test criterion in general form. The volume of the contaminated aquifer source zone is given by

$$V = L_x L_y L_z \tag{3.1}$$

where L_x is the dimension of the contaminated aquifer source zone parallel to flow (cm)
L_y is the horizontal dimension of the contaminated aquifer source zone perpendicular to flow (cm)
L_z is the vertical dimension of the contaminated aquifer source zone perpendicular to flow (cm).

Substituting Equation 3.1 into Equation 2.1 the test criterion can be rewritten as

$$M_i - (\theta_w C_{wi}^{sol} + \theta_a C_{vi}^{sat} + \beta K_{di} C_{wi}^{sol}) \cdot L_x \cdot L_y \cdot L_z > 0 \tag{3.2}$$

Note that because the source zone is in an aquifer (where the volumetric air content is zero, the volumetric water content is equal to the total porosity, and the bulk density of the solid sorbent is more appropriately defined as the soil bulk density), Equation 3.2 is equivalent to

$$M_i - (\theta_t C_{wi}^{sol} + \beta_s K_{di} C_{wi}^{sol}) \cdot L_x \cdot L_y \cdot L_z > 0 \tag{3.3}$$

where θ_t is the total porosity of the soil (unitless)
β_s is the soil bulk density for an aquifer or vadose zone (g cm^{-3}).

Equation 3.3 is the test criterion that the module actually uses for contaminated aquifer simulations.

Because all contaminant masses and loss fluxes are updated within a time step (before the numerical solution algorithm proceeds to the next time step) the module also has a complete record of contaminant mass produced in a time step based on chain decay of some parent species. This new mass is included in the total mass for that contaminant for the next time step.

3.1 Mass Loss Expressions for Individual or Multiple Concurrent Loss Routes

The processes that can cause contaminant mass (or activity) to be lost from the source zone are assumed to be first-order radioactive decay/degradation within the source zone and horizontal leaching of the contaminant from the source zone along with the flowing groundwater. Hence, the overall instantaneous rate of change of contaminant mass in the source zone for contaminant *i* is given by

$$\frac{dM_i}{dt} = \left[\frac{dM_i}{dt}\right]_{\text{decay}} + \left[\frac{dM_i}{dt}\right]_{\text{leach}} \tag{3.4}$$

This section discusses the theory developed to describe the individual terms of the right-hand side of Equation 3.4.

3.1.1 First-Order Decay

The radioactive decay/degradation process is assumed to follow first-order kinetics, which means that the rate of loss of mass at any given time is directly proportional to the mass present at that time. The mass flux equation for loss from the source zone by decay/degradation is then given by

$$\left[\frac{dM_i}{dt}\right]_{\text{decay}} = -\lambda_i M_i \tag{3.5}$$

where λ_i is the first-order decay/degradation coefficient for contaminant *i* (yr^{-1})

This equation applies if decay/degradation is the only loss process, and also if the horizontal leaching process is occurring simultaneously.

Each contaminant is assumed to have a unique overall first-order decay coefficient λ_i. Note that Equation 3.5 is based on the assumption that the first-order decay coefficient is independent of which phase (aqueous, solid-sorbent, or NAPL) the contaminant resides in.

3.1.2 Leaching

The leaching process is assumed to occur by advective transport of the contaminant out of the downgradient face of the source zone. This means that the rate of loss of mass at any given time is given by the volumetric flux of water out of the source zone face multiplied by the concentration of the contaminant in the water at that time:[a]

$$\left[\frac{dM_i}{dt}\right]_{leach} = - Q_w \, C_{wi} \tag{3.6}$$

where Q_w is the volumetric flux of water flowing through the aquifer source zone or vadose zone source zone, or out of the bottom of a pond/surface impoundment source zone ($cm^3 \, yr^{-1}$).

The volumetric water flux, in turn, can be expressed in terms of the Darcy water flux density (i.e., Darcy velocity) and the area of the downgradient face of the source zone:

$$Q_w = q_w \, L_y \, L_z \tag{3.7}$$

where q_w is the Darcy flux density of water flowing through the aquifer or vadose zone ($cm \, yr^{-1}$).

By substituting Equation 3.7 into Equation 3.6, the mass flux equation for loss from the source zone by leaching can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = - q_w \, L_y \, L_z \, C_{wi} \tag{3.8}$$

Again, this equation applies if leaching is the only loss process, and also if decay/degradation is occurring simultaneously.

When a NAPL phase exists in the source zone, the aqueous concentration of the contaminant is controlled by the composition of the NAPL phase. In this case, the source-term release module calculates the value of C_{wi} in Equation 3.8 by the phase partitioning theory described in Section 2.2.4 (which uses different methods, depending on the mole fraction [or concentration] of the contaminant in the NAPL phase).

When no NAPL phase exists in the source zone, the aqueous concentration can be calculated by a simple phase partitioning relation (i.e., Equation 2.7 in Section 2.2.3). Substituting Equation 3.1 into Equation 2.7, and explicitly noting that the volumetric water content is equal to the total porosity for a contaminated aquifer source zone, the aqueous concentration can be given by

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[a] Note that, in a strict sense, the variable Q_w should really be referred to as the aqueous solution flux (which contains water and dissolved constituents). However, because aqueous solutions are typically volumetrically dilute with respect to their dissolved constituents, it is quite common to refer to the aqueous solution flux as the water flux.

$$C_{wi} = \frac{M_i}{\theta_t \, R_i \, L_x \, L_y \, L_z} \tag{3.9}$$

Now, substituting Equation 3.9 into Equation 3.8, the mass flux equation for loss from the source zone by leaching (when no NAPL is present) can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\frac{q_w \, M_i}{\theta_t \, R_i \, L_x} \tag{3.10}$$

Recall that the retardation factor, R_i, that appears in Equation 3.10 was defined in general terms by Equation 2.5. It is worthwhile to note that for the contaminated aquifer source zone, the volumetric water content and solid-sorbent bulk density in Equation 2.5 are equal to the total porosity, θ_t, and soil bulk density, β_s, respectively.

3.2 Special Cases with Analytical Solutions

For scenarios where the contaminant only exists in the aqueous or solid-sorbent phases and where no contaminant decays into another contaminant, the individual mass loss terms are given by Equations 3.5 and 3.10. When these are substituted into Equation 3.4, the total mass loss rate can be expressed as

$$\frac{dM_i}{dt} = -\lambda_i M_i - \frac{q_w M_i}{\theta_t R_i L_x} = -\left(\lambda_i + \frac{q_w}{\theta_t R_i L_x}\right) M_i \tag{3.11}$$

The analytical solution to Equation 3.11 is

$$M_i(t) = M_{io} \exp\left[-\left(\lambda_i + \frac{q_w}{\theta_t R_i L_x}\right)\right] \tag{3.12}$$

where M_{io} is the initial total mass or activity of contaminant *i* in the source zone (g or Ci), and exp[•] is the exponential function.

Equation 3.12 could be substituted into Equations 3.5 and 3.10 to produce analytical expressions for the individual mass loss rates as well. Equations 3.5, 3.10, and 3.12 could then be used to verify the outputs of the source-term release module for these scenarios, if none of the contaminants decay/degrade into other species of concern (e.g., other contaminants in the initial source inventory). If they do, this set of analytical solutions will not capture the entire decay-chain behavior (as the numerical procedure will).

3.3 Numerical Solution Procedure for the General Case

In the general case of multiple, concurrent, contaminant loss routes, an analytical solution to Equation 3.4 is not always possible for the following reasons. Firstly, if a NAPL phase is present in the source zone, the leaching term cannot be expressed as a single, simple function of M_i and t. Secondly, even if a NAPL phase did not exist, the leaching term may be an arbitrary function of time. By this we mean that the Darcy water flux density in the aquifer (for the scenario under study) may vary in time due to natural phenomena or the implementation of remediation methodologies. The user has the ability to enter the Darcy water flux density in the aquifer as a time series of discrete values. There are no hard limits on the number of elements constituting the time series used to describe such a parameter. The code will allocate available memory as it is needed. Therefore any arbitrary transient Darcy water velocity can be accommodated, provided memory and run time limits are not exceeded.

Equation 3.4 can be represented by the general form:

$$\frac{dM_i}{dt} = f_1(M_i,t) + f_2(M_i,t) = f(M_i,t) \tag{3.13}$$

where $f(\bullet)$, $f_1(\bullet)$, and $f_2(\bullet)$ are generic representation of functions.

The source-term release module solves this first-order, ordinary differential equation numerically by using a fourth-order Runge-Kutta method. This method requires four computations of the function $f(\bullet)$ for each time step (Δt). However, one of the benefits of this method over other methods is that a larger time step can be used while keeping the error below some desired level. This method has an accumulated error on the order of (Δt). This means that if you cut the time step in half, you decrease the error by a factor of 16. In comparison, if Euler's method was used, cutting the time step in half would only decrease the error by a factor of 2. The Runge-Kutta method can therefore use a much larger time step than the Euler method, which will more than compensate for the extra computations required per time step.

The numerical solution algorithm begins at time $t = 0$ with $M_i = M_{io}$. The Runge-Kutta algorithm for updating contaminant mass over the course of a time step is given by

$$M_i(t_{n+1}) = M_i(t_n) + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \tag{3.14}$$

where the terms in Equation 3.14 are given by

$$k_1 = \Delta t\, f(M_i(t_n), t_n) \tag{3.15}$$

$$k_2 = \Delta t\, f\left(M_i(t_n) + \frac{k_1}{2}, t_n + \frac{\Delta t}{2} \right) \tag{3.16}$$

$$k_3 = \Delta t\, f\left(M_i(t_n) + \frac{k_2}{2}, t_n + \frac{\Delta t}{2} \right) \tag{3.17}$$

$$k_4 = \Delta t\, f(M_i(t_n) + k_3, t_n + \Delta t) \tag{3.18}$$

where $M_i(t_n)$ is the value of M_i at time $n\Delta t$, and t_n is the time $n\Delta t$.

The value of M_i is therefore updated in a stepwise fashion over finite intervals of time.

Note that because the function $f(\bullet)$ can be expressed as the sum of the functions $f_1(\bullet)$ and $f_2(\bullet)$ (from Equation 3.13), the Runge-Kutta procedure used to update the total contaminant mass in the source zone (described in Equations 3.14 - 3.18) contains calculations of the k_1 through k_4 terms that would be associated with the individual functions $f_1(\bullet)$ and $f_2(\bullet)$. Because these functions are associated with the individual mass loss terms, the numerical scheme allows us to also obtain the individual mass fluxes to each loss route at discrete times with minimal extra computation. This entire procedure is repeated as long as not all of the contaminant mass has been depleted from the source zone.

3.4 Methods for Calculating Selected Parameters in the Mass Loss Expressions

The first order decay/degradation coefficient is related to radioactive decay and degradation. The RAAS and MEPAS databases contain decay half lives for radionuclides and degradation half lives for some non-radioactive contaminants. If values of half life are available, the decay constant is calculated as

$$\lambda_i = \frac{\ln(2)}{t_{\frac{1}{2}i}} \tag{3.19}$$

where $t_{1/2i}$ is the decay/degradation half life of contaminant *i* in any phase (yr).

3.5 Using Known Fluxes

For the contaminated aquifer case, the known flux capabilities of the module can be applied to leaching only. Known flux capabilities can be used in two ways. The first way to use known fluxes would be to pass known leaching flux rates to the groundwater transport code. The second way would be to "turn leaching off" by inputting a known leaching flux of 0. The overall treatment of mass loss in the source-term module does not change. The known leach rate replaces the calculated value for $[dM_i/dt]_{leach}$ in Equation 3.4. All other calculations are done identically to the calculated flux cases.

4.0 Contaminated Pond/Surface Impoundment

Consider that the contaminated source zone is a pond or surface impoundment on the surface of the vadose zone soil. The source-term release module conceptualizes this zone to be a rectangular parallelopiped with volume V, horizontal cross-sectional area A, and depth d_p.

It is assumed that the pond or surface impoundment consists primarily of water (i.e., it is primarily an aqueous phase rather than being a NAPL-phase mixture). However, there may be small globules of NAPL phase suspended in the water, if the masses of any of the contaminants that may partition into a NAPL phase are above the saturation limit of the pond water. (In other words, the pond may be a sparse emulsion of NAPL in water.) Furthermore, it is assumed that the pond contains suspended sediment, which can act as a solid-sorbent phase for the contaminants. In addition, it is also assumed that the aqueous solubilities of all contaminants are low enough that contaminants present in the aqueous solution always exist as "dilute" constituents of that solution (and therefore behave that way with respect to volatilization theory). The source zone is assumed to be a so-called "well-mixed reactor," which means that its properties are spatially uniform throughout.

The contaminated pond/surface impoundment source zone is considered to not include a layer of contaminated sorbing sediment at the bottom of the pond. Any layer of contaminated sediment at the bottom of the pond should be treated as separate source zone for the current version of the source-term release module.(a)

Water is assumed to leave the pond by leaching into the vadose zone below the pond and by runoff from the top of the pond (and also possibly by evaporation from the pond surface). Water is assumed to be added to the pond by natural precipitation or run-on. No anthropogenic additions of water are assumed to occur. Furthermore, it is assumed that the net rate of water addition is just equal to the net rate of water loss, which means that V, A, and d_p can be considered constant in time.

It is assumed that suspended sediment particles do not leave the pond along with the water that leaches into the vadose zone (i.e., sediment particles would be filtered out of the water as it percolates into the soil at the bottom of the pond, and they would subsequently be resuspended into the pond rather than build up as a bottom sediment layer). However, suspended sediment particles are assumed to leave the pond with the runoff water. Similarly, run-on water is assumed to carry additional sediment particles into the pond. Furthermore, we will assume that the net rate of sediment particle addition is just equal to the net rate of sediment particle loss; which means that the concentration of suspended sediment in the pond, β_{ss}, can be considered constant in time.

The water lost by leaching and runoff will contain contaminants. (Water evaporating from the pond surface will be pure.) It is assumed that the water additions to the pond will not contain contaminants. It

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(a) Note that this is different than the way previous versions of MEPAS conceptualized a pond.

is further assumed that the water being lost to runoff will contain contaminated suspended sediment and suspended NAPL-phase globules, in addition to the dissolved contaminant. Water that leaches into the vadose zone from the bottom of the pond is assumed to contain only dissolved contaminants (i.e., NAPL-phase globules would also be filtered out of the water as it percolates into the soil at the bottom of the pond, and they would subsequently be resuspended into the pond rather than build up as a continuous pool).

Section 2.2.2 describes how the source-term release module tests to determine if a NAPL phase exists (based on the current masses of contaminants in the source zone) at the beginning of each time step. Equation 2.1 in Section 2.2.2 is the test criterion in general form. The volume of the contaminated pond/surface impoundment source zone is given by

$$V = A\, d_p \tag{4.1}$$

where	A	is the horizontal cross-sectional area of the contaminant source zone (cm^2)
	d_p	is the depth of the pond (cm).

Substituting Equation 4.1 into Equation 2.1 the test criterion can be rewritten as

$$M_i - (\theta_w C_{wi}^{sol} + \theta_a C_{vi}^{sat} + \beta K_{di} C_{wi}^{sol}) \cdot A \cdot d_p > 0 \tag{4.2}$$

Note that because the source zone is a pond/surface impoundment (where the volumetric air content is zero and the bulk density of the solid sorbent is more appropriately defined as the suspended sediment concentration), Equation 4.2 is equivalent to

$$M_i - (\theta_w C_{wi}^{sol} + \beta_{ss} K_{di} C_{wi}^{sol}) \cdot A \cdot d_p > 0 \tag{4.3}$$

where β_{ss} is the concentration of suspended sediment in the pond water ($g\ cm^{-3}$).

Equation 4.3 is the test criterion that the module actually uses for contaminated pond/surface impoundment simulations.

Because all contaminant masses and loss fluxes are updated within a time step (before the numerical solution algorithm proceeds to the next time step) the module also has a complete record of contaminant mass produced in a time step based on chain decay of some parent species. This new mass is included in the total mass for that contaminant for the next time step.

4.1 Mass Loss Expressions for Individual or Multiple Concurrent Loss Pathways

The processes that can cause contaminant mass (or activity) to be lost from the source zone are assumed to be first-order radioactive decay/degradation within the pond, vertical leaching into the vadose zone below the pond, runoff from the top of the pond to the overland flow pathway, and volatilization from the surface of the pond. Hence the overall instantaneous rate of change of contaminant mass in the source zone for contaminant *i* is given by

$$\frac{dM_i}{dt} = \left[\frac{dM_i}{dt}\right]_{decay} + \left[\frac{dM_i}{dt}\right]_{leach} + \left[\frac{dM_i}{dt}\right]_{over} + \left[\frac{dM_i}{dt}\right]_{vol} \tag{4.4}$$

This section discusses the theory developed to describe the individual terms on the right-hand side of Equation 4.4.

4.1.1 First-Order Decay

The radioactive decay/degradation process is assumed to follow first-order kinetics, which means that the rate of loss of mass at any given time is directly proportional to the mass present at that time. The mass flux equation for loss from the source zone by decay/degradation is then given by

$$\left[\frac{dM_i}{dt}\right]_{decay} = -\lambda_i M_i \tag{4.5}$$

This equation applies if decay/degradation is the only loss process, and also if the other processes are occurring simultaneously.

Each contaminant is assumed to have a unique overall first-order decay coefficient λ_i. Note that Equation 3.5 is based on the assumption that the first-order decay coefficient is independent of which phase (aqueous, solid-sorbent, or NAPL) the contaminant resides in.

4.1.2 Leaching

The leaching process is assumed to occur by advective transport of the aqueous contaminant out of the bottom face of the pond along with the infiltrating pond water (i.e., no contaminated suspended sediment or NAPL-phase globules leach). This means that the rate of loss of mass at any given time is given by the volumetric flux of water out of the source zone face multiplied by the aqueous concentration of the contaminant in the water at that time:[(a)]

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\ Q_w\ C_{wi} \tag{4.6}$$

The volumetric water flux, in turn, can be expressed in terms of the Darcy water flux density (i.e., Darcy velocity) of the infiltrating water and the area of the bottom face of the source zone:

$$Q_w = q_w\ A \tag{4.7}$$

By substituting Equation 4.7 in Equation 4.6, the mass flux equation for loss from the source zone by leaching can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\ q_w\ A\ C_{wi} \tag{4.8}$$

Again, this equation applies if leaching is the only loss process, and also if the other processes are occurring simultaneously.

When suspended globules of a NAPL phase exist in the pond, the aqueous concentration of the contaminant is controlled by the composition of the NAPL phase. In this case, the source-term release module calculates the value of C_{wi} in Equation 4.8 by the phase partitioning theory described in Section 2.2.4 (which uses different methods, depending on the mole fraction [or concentration] of the contaminant in the NAPL phase).

When no suspended globules of a NAPL phase exist in the pond, the aqueous concentration can be calculated by a simple phase partitioning relation (i.e., Equation 2.7 in Section 2.2.3). Substituting Equation 4.1 into Equation 2.7, the aqueous concentration can be given by

$$C_{wi} = \frac{M_i}{\theta_w R_i A\, d_p} \tag{4.9}$$

(a) Note that, in a strict sense, the variable Q_w should really be referred to as the aqueous solution flux (which contains water and dissolved constituents). However, because aqueous solutions are typically volumetrically dilute with respect to their dissolved constituents, it is quite common to refer to the aqueous solution flux as the water flux.

Now, substituting Equation 4.9 into Equation 4.8, the mass flux equation for loss from the source zone by leaching (when no NAPL is present) can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = - \frac{q_w M_i}{\theta_w R_i d_p} \tag{4.10}$$

Recall that the phase apportionment factor, R_i, that appears in Equation 4.10 was defined in general terms by Equation 2.5. It is worthwhile to note that for the contaminated pond/surface impoundment source zone, the "volumetric water content" will be very close to one, and solid-sorbent bulk density in Equation 2.5 is equal to the suspended sediment concentration, β_{ss}.

4.1.3 Overland Flow (Runoff)

The overland flow loss process is assumed to occur by runoff from the surface of the pond/surface impoundment. Because we are assuming that the aqueous solution, the suspended sediment, and the suspended NAPL-phase globules (if present) all are lost from the pond in the runoff process, the mass flux equation for loss from the pond by overland flow (either alone or simultaneous with the other processes) can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{over} = - Q_{over} C_{Ti} \tag{4.11}$$

where Q_{over} total flux of aqueous solution, sediment, and NAPL globules as pond runoff ($cm^3\ yr^{-1}$).

Note that in Equation 4.11, Q_{over} is not just the volumetric flux of water (or aqueous solution) leaving the pond as runoff, but rather it is the total volumetric flux of aqueous solution, sediment, and NAPL-phase globules (if present) leaving the pond as runoff.

Substituting Equation 4.1 into Equation 2.2, to obtain a specific expression for the overall total contaminant concentration in a pond/surface impoundment source zone, and then substituting the resulting expression into Equation 4.11, we can rewrite the mass flux equation for loss from the pond by overland flow (either alone or simultaneous with the other processes) as

$$\left[\frac{dM_i}{dt}\right]_{over} = - \frac{Q_{over} M_i}{A\, d_p} \tag{4.12}$$

4.1.4 Volatilization

It is assumed that contaminants in the pond/surface impoundment volatilize into the atmosphere above the pond only from the aqueous phase (i.e., no contaminants volatilize directly from the surface of suspended sediment particles or NAPL-phase globules that may be located at the surface of the pond and that may periodically be in contact with the atmosphere). This seems to be a reasonable assumption because the vast majority of the pond surface should be an air-water interface rather than a sediment-air or globule-air interface. With this assumption, and the fact that the contaminants are assumed to be dilute constituents of the aqueous phase, standard theory (USEPA 1988a, 1990) for volatilization from the surface of a water body should apply. This theory is based on the "two-resistance" model (Thibodeaux 1979; Hwang 1982; Mackay and Leinonen 1975) which assumes that the controlling mechanisms for volatilization from the bulk solution to the atmosphere are the diffusion resistances of thin transition layers in the liquid phase and the gas phase located at the air-water interface. Based on this theory, the mass flux equation for loss from the pond/surface impoundment by volatilization (either alone or simultaneous with the other processes) can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = - A\, K_{li}\, C_{wi} \tag{4.13}$$

where K_{li} is the overall mass transfer coefficient from a liquid phase to the atmosphere for contaminant *i*, expressed in terms of the liquid-phase concentration (cm yr^{-1}).

When suspended globules of a NAPL phase exist in the pond, the aqueous concentration of the contaminant is controlled by the composition of the NAPL phase. In this case, the source-term release module calculates the value of C_{wi} in Equation 4.13 by the phase partitioning theory described in Section 2.2.4 (which uses different methods, depending on the mole fraction [or concentration] of the contaminant in the NAPL phase).

When no suspended globules of a NAPL phase exist in the pond, the aqueous concentration can be calculated by a simple phase partitioning relation (i.e., Equation 4.9). Now, substituting Equation 4.9 into Equation 4.13, the mass flux equation for contaminant loss (when no NAPL is present) from the pond/surface impoundment by volatilization (either alone or simultaneous with the other processes) can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{vol} = - \frac{K_{li}\, M_i}{\theta_w\, R_i\, d_p} \tag{4.14}$$

The expressions in Equations 4.13 and 4.14 represent instantaneous rates of mass loss at a specific time (just like the expressions for all other mass loss term presented thus far). However, during the course of testing the source-term release module, it was discovered that for certain more volatile compounds, these expressions caused all of the initial contaminant inventory to be lost to volatilization in the first time step (which was 1 yr for those runs). It was hypothesized that the reason for this was that a 1-yr time step was too large for the Runge-Kutta numerical solution for volatilization. However, applications of RAAS/MEPAS often simulate scenarios that cover an extremely long time period (e.g., 10,000 yr). So, using a time step significantly smaller than 1 yr would cause undesirably long run times. In addition, modifying the numerical solution algorithm to use variable-length time steps, the size of which would be determined by limits on the magnitude of contaminant mass that could be lost in any given time step, was deemed beyond the scope of the current version of the source-term release module.

The approach taken to compensate for these high volatilization loss predictions was to use a mass loss expression that was time-averaged over the time step (rather than instantaneous). This will reduce the predicted flux because the time-averaged expression accounts for the fact that the flux decreases over time as the aqueous concentration decreases. One simplifying assumption made is that the time-averaged formula for volatilization loss can be derived by assuming that volatilization is the only process contributing to loss over the time step. Another simplifying assumption made is that aqueous contaminant is not replenished by desorption from suspended sediment or dissolution from the NAPL phase as it is decreased through volatilization. This latter assumption must be made because the complex phase partitioning theory required when a NAPL phase is present precludes deriving an analytical expression for the time-averaged mass loss.

Mackay and Leinonen (1975) began with an expression similar to Equation 4.13, and derived a transient-state expression for volatilization from a pond where only aqueous contaminant is present that was applicable for times t = 0 to t = t. . The analogous transient-state expression applicable for times between the beginning and end of a time step (of size Δt), is

$$\left[\frac{dM_i}{dt}\right]_{vol} = - A\ K_{li}\ C_{wi}\ \exp\left(- \frac{K_{li}}{\theta_w\ d_p}\ t\right) \tag{4.15}$$

In Equation 4.15, C_{wi} should be interpreted as the concentration at the beginning of the time step, and t should be interpreted as the length of time from the beginning of the time step. As stated above, if we assume that only aqueous mass changes during the time step, Equation 4.15 can be averaged over the time step to obtain

$$\left[\frac{dM_i}{dt}\right]_{vol}^{ave} = - \frac{A\ d_p\ C_{wi}}{\Delta t}\left[1 - \exp\left(- \frac{K_{li}}{d_p}\Delta t\right)\right] \tag{4.16}$$

Note that when K_{li} is small, Equation 4.16 reduces to Equation 4.13; which means that using Equation 4.16 for compounds that are not highly volatile (for which there was no problem with the instantaneous mass loss expressions) is equivalent to using the instantaneous mass loss expressions.

So, when suspended globules of a NAPL phase exist in the pond, the module actually uses Equation 4.16, coupled with phase partitioning theory to determine C_{wi}. When no suspended globules of a NAPL phase exist in the pond, the module actually uses

$$\left[\frac{dM_i}{dt}\right]_{vol}^{ave} = -\frac{M_i}{\Delta t\,\theta_w R_i}\left[1 - \exp\left(-\frac{K_{li}}{d_p}\Delta t\right)\right] \tag{4.17}$$

which is the analogue of Equation 4.14 (and reduces to it when K_{li} is small [or, more precisely, when the argument of the exponential function on the right-hand side of Equation 4.17 is small]).

4.2 Special Cases with Analytical Solutions

For contamination scenarios where the contaminant only exists in either the aqueous or solid-sorbent phases, where no contaminant decays into another contaminant, and when time-averaging of the *volatilization* term is not needed, the individual mass loss terms are given by Equations 4.5, 4.9, 4.12, and 4.14. When these are substituted into Equation 4.4, it becomes

$$\frac{dM_i}{dt} = -\left(\lambda_i + \frac{q_w}{\theta_w R_i d_p} + \frac{Q_{over}}{A\,d_p} + \frac{K_{li}}{\theta_w R_i\,d_p}\right) M_i \tag{4.18}$$

The analytical solution to Equation 4.18, for an initial contaminant mass of M_{io}, is

$$M_i(t) = M_{io}\,\exp\left[-\left(\lambda_i + \frac{q_w}{\theta_w R_i d_p} + \frac{Q_{over}}{A\,d_p} + \frac{K_{li}}{\theta_w R_i\,d_p}\right) t\right] \tag{4.19}$$

Equation 4.19 could be substituted into Equations 4.5, 4.9, 4.12, and 4.14 to produce analytical expressions for the individual mass loss rates as well. Equations 4.5, 4.9, 4.12, 4.14, and 4.19 could then be used to verify the outputs of the source-term release module for these scenarios, if none of the contaminants decay/degrade into other species of concern (e.g., other contaminants in the initial source inventory). If they do, this set of analytical solutions will not capture the entire decay-chain behavior (as the numerical procedure will).

4.3 Numerical Solution Procedure for the General Case

In the general case of multiple, concurrent, contaminant loss routes, an analytical solution to Equation 4.4 is not always possible. The reasons for this are similar to those discussed for the contaminated aquifer source zone (e.g., complex NAPL partitioning theory, time-varying parameters). The numerical solution algorithm is identical to that described in Section 3.3 (for the contaminated aquifer), so the reader is referred there for details.

4.4 Methods for Calculating Selected Parameters in the Mass Loss Expressions

The first order decay/degradation coefficient is related to radioactive decay and degradation. The RAAS and MEPAS databases contain decay half-lives for radionuclides and degradation half-lives for some non-radioactive contaminants. If values of half life are available, the decay coefficient is calculated by

$$\lambda_i = \frac{\ln(2)}{t_{\frac{1}{2}i}} \tag{4.20}$$

For all volatilization related calculations, the module uses the modified Henry's Law constant (unitless). The Henry's Law constant is obtained from the contaminant database and multiplied to obtain the unitless version by

$$K_{Hi} = \frac{H_i}{R \cdot T} \tag{4.21}$$

where H_i is the Henry's Law constant for contaminant *i* (press./concen. basis) (atm m^3 mol^{-1})
R is the Universal gas constant (atm L mol^{-1} K^{-1})
T is the absolute temperature (K).

The overall mass transfer coefficient, K_{li}, in Equations 4.13 and 4.14 is calculated by the source-term release module. This calculation is (Hwang 1982)

$$\frac{1}{K_{li}} = \frac{1}{k_{il}} + \frac{1}{K_{Hi} k_{ig}} \tag{4.22}$$

where k_{il} is the liquid-phase mass transfer coefficient for contaminant *i* at a pond surface (cm yr^{-1})
k_{ig} is the gas-phase mass transfer coefficient for contaminant *i* at a pond surface (cm yr^{-1}).

These mass transfer coefficients are calculated as follows (Hwang 1982):

$$k_{il} = \left(\frac{M_{mO_2}}{M_{mi}}\right)^{0.5} \left(\frac{T}{298}\right) k_{O_2,1} \tag{4.23}$$

$$k_{ig} = \left(\frac{M_{mH_2O}}{M_{mi}}\right)^{0.335} \left(\frac{T}{298}\right)^{1.005} k_{H_2O,g} \tag{4.24}$$

4.5 Using Known Fluxes

For the pond/surface impoundment case, the known flux capabilities of the module can be applied to leaching, overland flow, and volatilization. Known flux capabilities can be used in two ways for each pathway. The first way to use known fluxes for leaching would be to pass known leaching flux rates to the groundwater transport code. The second way would be to "turn leaching off" by inputting a known leaching flux of 0. The same is true for the overland pathway and the volatilization pathway. The volatilization pathway offers an additional method for adjusting flux. An adjustment factor (called the volatization ratio) can be multiplied by $[dM_i/dt]_{vol}$ to reduce the volatization flux. The overall treatment of mass loss in the source-term module does not change. The known leach rate replaces the calculated value for $[dM_i/dt]_{leach}$, the known overland rate replaces the calculated $[dM_i/dt]_{over}$, and the known volatization rate replaces the calculated $[dM_i/dt]_{vol}$ in Equation 4.4. All other calculations are done identically to the calculated flux cases.

5.0 Contaminated Vadose Zone

The theory previously presented for the contaminated aquifer (Section 3.0) and pond/surface impoundment (Section 4.0) source zones is relatively straightforward because no synergistic or antagonistic interactions between loss processes occur, and because the source zone dimensions remain constant. On the other hand, the theory presented here for the contaminated vadose zone source zone is relatively complex. Firstly, auxiliary theory implemented in the source-term release module to calculate selected parameters used in the vadose zone mass loss equations is relatively extensive. Because of this, this section begins with separate subsections giving detailed descriptions of theory related to water balance calculations, wind emissions calculations, and overland sediment loss calculations. Secondly, synergistic and antagonistic interactions between contaminant loss processes do occur in the general vadose zone source zone scenario. Therefore, for clarity, this section first presents derivations of mass loss expressions for individual processes (assuming they are acting alone), and then presents derivations of the mass loss expressions when interactions can occur. Thirdly, three of the possible loss processes may cause the dimensions of the source zone to change. This time variation of source zone dimensions complicates the mass loss theory, and requires a more involved numerical solution procedure. Fourthly, this section also discusses two types of remediation methodologies for contaminated vadose zones for which special theory has been implemented. And finally, the nature of volatilization in a vadose zone is more complex in and of itself.

There are many different possible types of vadose zone source zones; and the volatilization from different types of sources may be controlled by different mechanisms or combinations of mechanisms. Furthermore, for certain specific types of contamination sources, the mechanisms controlling contaminant volatilization may change over time (as the source zone changes over time) and may be different for different contaminants or contaminant concentrations. Therefore, a complete description of each type of contaminant source may encompass one or more completely different types of volatilization model.

Each type of volatilization scenario may be described by unique volatilization theory (i.e., each may have a different equation that is appropriate for estimating the mass loss from the source zone as a function of time due to volatilization). For this reason, previous versions of MEPAS required the user to select one of a number of possible volatilization scenarios for a contaminated vadose zone. MEPAS then computed the emission rate based on idealized volatilization theory that was appropriate to that particular volatilization scenario, under the assumption that volatilization was the only loss process occurring. Each of these theories implicitly assumed that the contaminants were present either entirely in a NAPL phase, or that a NAPL phase never existed. In addition, the fundamental conceptualization of the source zone for some of these volatilization models was different than that for models of other loss processes. This was not a problem as long as loss routes were analyzed independently; but it is a problem for a source-term release module where mass-balanced, coupled loss theory is required. Currently, only one hybrid-type of volatilization scenario has been implemented in the source-term release module for a vadose zone source zone. The basis of this scenario was the so-called "Land Treatment Facilities" case of the previous configuration of MEPAS (see Droppo and Buck 1996). However, the theory for this scenario has been greatly enhanced to accommodate source zones with or without a NAPL phase (or that contain a NAPL phase initially that disappears during the course of the simulation). The theory is commensurate with multiple interactive loss process and complex NAPL phase partitioning.

Consider that the contaminated source zone is located somewhere in the vadose zone. The source-term release module conceptualizes this zone to be a rectangular parallelopiped with horizontal cross-sectional area A. There may be a layer of uncontaminated soil above the source zone initially. The position of the soil surface (i.e., the upper boundary of the vadose zone) may recede over time because of wind suspension or water erosion of particles. The bottom of the source zone always remains at the same location. However, the top of the source zone may recede (to lower elevations) over time because of the aforementioned wind suspension or water erosion processes, or because of volatilization. Therefore, the thickness of the source zone, h, and its volume, V, may vary over time.

The source zone contains an aqueous phase (the vadose zone pore water), a vapor phase (the air-filled pore space), a solid-sorbent phase (the soil matrix), and may contain a NAPL phase (if the masses of any of the contaminants that may partition into a NAPL phase are above the saturation limits of the other two phases). The source zone is assumed to be a so-called "well-mixed reactor," which means that its properties are assumed to be spatially uniform throughout, for all mass loss theory except for the case of an ISS waste form. (However, there is one vadose zone scenario where a simplified spatial-gradient expression for volatilization is used as a bounding value when the primary theory would predict unphysically high loss rates.)

Section 2.2.2 describes how the source-term release module tests to determine if a NAPL phase exists (based on the current masses of contaminants in the source zone) at the beginning of each time step. Equation 2.1 in Section 2.2.2 is the test criterion in general form. The test criterion that the module actually uses for the contaminated vadose zone source zone is obtained by expressing the source zone volume (that appears in Equation 2.1) in terms of other specific source zone parameters. This expression may be a time-varying function, and may be given by different formulae, depending on the interaction of the loss processes. Because this theory is developed only later in this section, the specific test criterion for NAPL phase existence will be reported at the end of Section 5.5.

Because all contaminant masses and loss fluxes are updated within a time step (before the numerical solution algorithm proceeds to the next time step) the module also has a complete record of contaminant mass produced in a time step based on chain decay of some parent species. This new mass is included in the total mass for that contaminant for the next time step for all scenarios except for the scenario where the vadose zone has been subjected to an ISS remediation methodology. For this case, the special theory needed requires that the accumulation and subsequent loss of daughter products of concern be handled in a different manner (discussed explicitly below).

5.1 The Water Balance

The water balance is computed based on the method proposed by Thornthwaite and Mather (1955, 1957), Fenn et al. (1975), and Dass et al. (1977), and used by Whelan et al. (1987). The method involves a monthly water-balance calculation using meteorologic and site information, including monthly estimates of precipitation, potential evapotranspiration, snowmelt, temperature, and runoff. Long-term meteorological data needed for the water balance can be obtained from the Local Climatic Data (LCD) annual summaries published by the Environmental Data Service, National Oceanic and Atmospheric Administration (NOAA), National Climatic Data Center, U.S. Department of Commerce. Information for areas of the United States pertaining to each month is contained in the LCDs. The monthly tabulated data for 30 years of record are under "Normals, Means, and Extremes" in the LCDs.

5.1.1 Overview

The water balance is a mass balance of the flow and storage of water in surface soil on a per unit area basis, using the hydrologic equation: Inflow - Outflow = Change in Storage. The inflow is precipitation less overland runoff, the outflows are actual evapotranspiration (AET) and deep-drainage percolation, and water is stored as soil moisture. The wet season is that portion of the year where there is sufficient precipitation to satisfy potential evapotranspiration (PET), while in the dry season PET exceeds precipitation. The specific calculations in the monthly water balance are summarized in the following 9 steps:

- Adjusted Average Temperature - The temperature obtained from the LCD represents the average monthly temperature at the LCD station. Using adiabatic lapse rates, this temperature is adjusted for the elevation difference that may exist between the site and the LCD station. The elevation of the LCD station is listed in the LCD.

- Potential Evapotranspiration (PET) - The modified Blaney-Criddle method (Doorenbos and Pruitt 1977), the Penman method (Penman 1948) and the Penman method with correction factor (Doorenbos and Pruitt 1977) are used to estimate PET rate. All three methods are based on average air temperature, minimum relative humidity, ratio of actual to maximum possible sunshine hours, and average wind speed. The Penman method and Penman method with correction factor methods are also based on the maximum relative humidity and latitude. These parameters are contained in the LCD and are different than those used by Thornthwaite and Mather (1955, 1957), Fenn et al. (1975), and Dass et al. (1977). Because the soil moisture storage calculations are based on PET rate, the computation of PET rate has a significant influence on the amount of water that percolates into the waste site.

- Adjusted Precipitation - Monthly precipitation is obtained from the LCD. Precipitation occurring in months with an adjusted temperature below freezing is assumed to be in the form of snowfall. Snowfall is assumed to occur before any considerable ground-surface freezing has taken place. This assumption is important because when snowmelt occurs, percolation can also occur. It is also assumed that the snow is stored on the ground during the months when the adjusted average monthly temperature is below freezing. During the spring melt, a portion of the snowmelt is combined with the precipitation. This adjusted precipitation is used in the overland runoff and percolation computations. Snowmelt computations consider melt from rainfall, vapor condensation, convection, and radiation. Typically required parameters include average temperature, average wind speed, site elevation, mean sky cover (i.e., degree of cloudiness), and monthly precipitation as rainfall, all of which are contained in the LCD.

- Overland Runoff - The Soil Conservation Service (SCS) curve number technique forms the basis of estimating the net monthly overland runoff. This technique is described in a separate document (Whelan et al. 1987) and will not be discussed in detail here.

- Maximum and Potential Percolation - Maximum percolation represents the difference between adjusted precipitation and monthly overland runoff. Potential percolation represents the difference between the maximum percolation and the PET. For months with an adjusted temperature below freezing, both the maximum and potential percolation are zero.

- Accumulated Potential Water Loss - This step represents the potential soil moisture water loss during a year. It is computed using the potential percolation and the soil moisture retention tables provided by Thornthwaite and Mather (1957).

- Soil Moisture Storage - This step computes the moisture contained in the surface soil at the end of each month. In dry months (i.e., months where PET is greater than adjusted precipitation), soil moisture storage is computed using the accumulated potential water loss and the soil moisture retention tables provided by Thornthwaite and Mather (1957). In wet months (i.e., months where adjusted precipitation is greater than PET), the soil moisture storage is computed using the potential percolation and the previous month's soil moisture.

- Actual Evapotranspiration (AET) - Actual evapotranspiration equals PET, if the maximum percolation (i.e., adjusted precipitation less overland runoff) is greater than or equal to PET. If maximum percolation is less than PET, then there is not enough new moisture to entirely satisfy PET. Thus, AET will equal the sum of maximum percolation and the amount by which soil moisture storage is reduced (i.e., maximum percolation minus the change in soil moisture storage between the current and previous months).

- Deep-Drainage Percolation - The leachate generated from a soil column is zero if the adjusted temperature is below zero. If the temperature is above zero, the leachate generated equals the maximum percolation minus AET and change in soil moisture storage.

A complete description of the steps highlighted above is provided below in sections 5.1.2 through 5.1.9.(a)

(a) Many of the original equations in this chapter were developed using English units. For consistency, all parameters and equations are expressed in metric units, unless otherwise noted.

5.1.2 Adjusted Average Temperature

Temperatures obtained from the LCD are adjusted for the elevation difference that may exist between the LCD station and the actual site. In general, air temperatures decrease about 0.5 to 0.9°C per 100 m (3 to 5°F per 1000 ft) rise in altitude (Mockus 1971). Using the ideal gas law with the assumption of dry adiabatic conditions, Eagleson (1970) derived an approximate lapse rate (i.e., rate of change of temperature with height in the free atmosphere) of 1°C decrease per 100 m (5.5°F decrease per 1000 ft). This dry adiabatic lapse rate is a maximum rate (excluding superadiabatic conditions). A mean lapse rate as suggested by Linsley et al. (1975) is a decrease of about 0.7°C per 100 m (3.8°F per 1000 ft) of vertical rise. By using the mean lapse rate suggested by Linsley et al. (1975), the adjusted average monthly temperature is computed as follows:

$$T_{aj} = T_{uj} - 0.007(h_1 - h_0) \tag{5.1}$$

where T_{aj} is the adjusted average monthly temperature at the actual site for the *j*-th month (C)
T_{uj} is the unadjusted average monthly temperature at the LCD station for the *j*-th month (°C)
h_0 is the elevation of LCD station (m)
h_1 is the elevation of actual site (m).

5.1.3 Potential Evapotranspiration

Potential evapotranspiration is a critical parameter in the water balance. If the PET estimate is too high, then the volume of leachate will be underpredicted. If the PET estimate is too low, then overpredicted leachate-volume estimates may result. The estimated PET may not be high enough in arid regions, because most of the techniques used for estimating PET were not developed for arid regions.

Rosenberg (1974) notes that the concept of PET has been widely accepted, and he defines it as follows:

> "Potential evapotranspiration (PET) is the evaporation from an extended surface of short green . . . (vegetation) . . . which fully shades the ground, exerts little or negligible resistance to the flow of water, and is always well supplied with water. Potential evapotranspiration cannot exceed free water evaporation under the same weather conditions." (pp. 172)

He further notes that AET differs from PET under most circumstances. He attributes these differences to 1) the influence of surfaces that are not extended (i.e., great fetch), 2) varying heights in vegetation, 3) partial vegetative cover, 4) internal resistance in vegetation to water flow, 5) periodic water deficits (i.e., dry seasons during which vegetation is not well supplied with water), and 6) vegetation using more water in arid and dry regions than that suggested by pan evaporation (i.e., PET exceeding free water evaporation).

Rosenberg (1974) notes that in humid regions (i.e., where advection of sensible heat is unimportant) pan evaporation gives realistic estimates of PET. In arid localities and where advection is considerable, pan evaporation may give unrealistic values; in fact, he notes that the difference between pan evaporation and PET may be "very pronounced." In an effort to present a consistent methodology applicable uniformly throughout the country, PET rate is estimated in the module using well-accepted formulations (e.g., the Penman method), as opposed to being assumed equal to pan evaporation rate.

Doorenbos and Pruitt (1977) present four techniques for estimating PET rate: modified Blaney-Criddle method, Penman method with correction factor, Radiation method, and Pan Evaporation method. Gee and Simmons (1979) applied three of these techniques (i.e., modified Blaney-Criddle method, Penman method with correction factor, and radiation method) along with the original Penman formulation to the arid Pacific Northwest. Their results indicate that all methods yielded nearly the same cumulative PET over the 2-year simulation period except for the Penman method, which consistently overpredicted PET. Of the five methods mentioned above, the modified Blaney-Criddle method, Penman method, and Penman method with correction factor are used in MEPAS. The modified Blaney-Criddle method was chosen because it was developed for the arid western portions of the United States (Israelsen and Hansen 1962). The Penman method and Penman method with correction factor were chosen because Doorenbos and Pruitt (1977) believe that they offer the best results with the minimum possible error. All three methods are applied at each site, and the lowest PET estimate is used in that site's assessment. Note, this means that the highest estimate of leaching water flux (based on these three methods of PET estimation) is used by the source-term module. Therefore, because contaminant loss to leaching is maximized (relatively speaking), contaminant loss to other loss routes is correspondingly lower.

The methods used by the source-term release module to estimate PET are described below. The Penman method and Penman method with correction factor differ only by the correction factor. Thus, only the modified Blaney-Criddle method and Penman method with correction factor are described in this chapter.

Modified Blaney-Criddle Method

Blaney and Criddle (1950) calculated evapotranspiration from a consumptive-use factor, mean monthly temperature, and percentage of total annual daylight hours occurring during the period being considered (Doorenbos and Pruitt 1977). An empirically determined consumptive-use crop coefficient was then applied to establish evapotranspiration water requirements. Israelsen and Hansen (1962) note that this simplified formula was developed for the arid western portion of the United States and provides good estimates of seasonal water needs under these conditions. Doorenbos and Pruitt (1977) note that the effect of climate is insufficiently defined by considering only temperature and day length, because vegetative water requirements still vary widely among climates that exhibit similar temperatures and day lengths.

For a better definition of the effect of climate on vegetative requirements, Doorenbos and Pruitt (1977) present a modified version of the Blaney-Criddle technique. It includes monthly parameters, such as relative humidity, daytime wind speed, ratio of actual to maximum possible sunshine hours, temperature, latitude, and mean daily percentage of total annual daytime hours.

The method presented by Doorenbos and Pruitt (1977) as adapted for the module is summarized in the following governing equation:

$$E_{pj} = \begin{cases} f_j & \text{for } T_{aj} > 0°\text{C and } f_j < 2 \\ a_j + b_j \cdot f_j & \text{for } T_{aj} > 0°\text{C and } f_j \geq 2 \\ 0 & \text{for } T_{aj} \leq 0°\text{C} \end{cases} \tag{5.2}$$

in which

$$f_j = p_j \cdot (0.46\, T_{aj} + 8.13) \tag{5.3}$$

and

$$a_j = 0.0043 \cdot h^{rel}_{min(j)} - r_{sun(j)} - 1.41 \tag{5.4}$$

where

f_j	is a coefficient for Blaney-Criddle PET function for the *j*-th month (mm d^{-1})
a_j	is a coefficient for Blaney-Criddle PET function for the *j*-th month (mm d^{-1})
b_j	is a coefficient for Blaney-Criddle PET function for the *j*-th month (unitless)
p_j	*is the mean daily percentage of total annual daytime hours as a function of latitude for the j-*th month (unitless)
$h^{rel}_{min(j)}$	is the minimum percent relative humidity for the *j*-th month (unitless)
$r_{sun(j)}$	is the ratio of actual to maximum possible sunshine hours for the *j*-th month (unitless).

The coefficient b_j is a function of minimum relative humidity, ratio of actual to maximum possible sunshine hours, and mean daytime wind speed measured at a 2-m height, and is interpolated from Table 5.1. The coefficient p_j represents the mean daily percentage of total annual daytime hours and is interpolated from Table 5.2 for a given month and latitude.

In the source term release module, the ratio of actual to maximum possible sunshine hours is estimated from the mean sky cover (i.e., cloudiness) using the following equation (adapted from Doorenbos and Pruitt 1977):

$$r_{sun(j)} \approx 1 - 0.016\,(c_{sky(j)}) - 0.0084\,(c_{sky(j)})^2 \tag{5.5}$$

where $c_{sky(j)}$ is the mean sky cover for the *j*-th month obtained from the LCD (tenths) (unitless).

The mean daytime wind speed at a 2-m heightis estimated from the average wind speed for the month. The ratio between the mean daytime and nighttime wind speeds is approximately 2. Thus, the mean daytime wind speed corrected to a 2-m measurement height is obtained as follows (adapted from Doorenbos and Pruitt 1977):

$$U_{d2j} = 1.33 \cdot f_{hj} \cdot \overline{U}_j \tag{5.6}$$

in which

$$f_{hj} = \begin{cases} \left(\dfrac{2}{h_{in}}\right)^{0.17} & \text{for } h_{in} > 2 \\ \left(\dfrac{2}{h_{in}}\right)^{0.22} & \text{for } h_{in} \leq 2 \end{cases} \tag{5.7}$$

where U_{d2j} is the mean monthly daytime wind speed at a 2-m height for the *j*-th month (m s^{-1})
f_{hj} is the factor for the *j*-th month to correct the wind speed measurement to a 2-m measurement height (unitless)
$\overline{U}_j$ is the average wind speed for the *j*-th month, obtained from the LCD (m s^{-1})
h_{in} is the wind speed measurement height above ground (m).

In many instances, the height of the wind instruments above the ground (h_{in}) is included on a separate page of the LCD. If no information is available on h_{in}, assume 10 m (based on a typical meteorological tower).

Table 5.1. Prediction of b_j Factor for Different Conditions of Minimum Relative Humidity, Sunshine Duration, and Daytime Wind Speed (After Doorenbos and Pruitt 1977)

	$h^{rel}_{min(j)}$ (%)						
$r_{sun(j)}$	0	20	40	60	80	100	
0	0.84	0.80	0.74	0.64	0.52	0.38	U_{d2j} = 0 m/s
0.2	1.03	0.95	0.87	0.76	0.63	0.48	
0.4	1.22	1.10	1.01	0.88	0.74	0.57	
0.6	1.38	1.24	1.13	0.99	0.85	0.66	
0.8	1.54	1.37	1.25	1.09	0.94	0.75	
1.0	1.68	1.50	1.36	1.18	1.04	0.84	
0	0.97	0.90	0.81	0.68	0.54	0.40	U_{d2j} = 2 m/s
0.2	1.19	1.08	0.96	0.84	0.66	0.50	
0.4	1.41	1.26	1.11	0.97	0.77	0.60	
0.6	1.60	1.42	1.25	1.09	0.89	0.70	
0.8	1.79	1.59	1.39	1.21	1.01	0.79	
1.0	1.98	1.74	1.52	1.31	1.11	0.89	
0	1.08	0.98	0.87	0.72	0.56	0.42	U_{d2j} = 4 m/s
0.2	1.33	1.18	1.03	0.87	0.69	0.52	
0.4	1.56	1.38	1.19	1.02	0.82	0.62	
0.6	1.78	1.56	1.34	1.15	0.94	0.73	
0.8	2.00	1.74	1.50	1.28	1.05	0.83	
1.0	2.19	1.90	1.64	1.39	1.16	0.92	
0	1.18	1.06	0.92	0.74	0.58	0.43	U_{d2j} = 6 m/s
0.2	1.44	1.27	1.10	0.91	0.72	0.54	
0.4	1.70	1.48	1.27	1.06	0.85	0.64	
0.6	1.94	1.67	1.44	1.21	0.97	0.75	
0.8	2.18	1.86	1.59	1.34	1.09	0.85	
1.0	2.39	2.03	1.74	1.46	1.20	0.95	
0	1.26	1.11	0.96	0.76	0.60	0.44	U_{d2j} = 8 m/s
0.2	1.52	1.34	1.14	0.93	0.74	0.55	
0.4	1.79	1.56	1.32	1.10	0.87	0.66	
0.6	2.05	1.76	1.49	1.25	1.00	0.77	
0.8	2.30	1.96	1.66	1.39	1.12	0.87	
1.0	2.54	2.14	1.82	1.52	1.24	0.98	
0	1.29	1.15	0.98	0.78	0.61	0.45	U_{d2j} = 10 m/s
0.2	1.58	1.38	1.17	0.96	0.75	0.56	
0.4	1.86	1.61	1.36	1.13	0.89	0.68	
0.6	2.13	1.83	1.54	1.28	1.03	0.79	
0.8	2.39	2.03	1.71	1.43	1.15	0.89	
1.0	2.63	2.22	1.86	1.56	1.27	1.00	

Table 5.2. Prediction of p_j Factor for Different Months and Latitudes (After Doorenbos and Pruitt 1977)

	Latitude (degrees)										
Month	0	5	10	15	20	25	30	35	40	45	50
Jan	0.267	0.264	0.261	0.257	0.252	0.246	0.239	0.231	0.220	0.209	0.195
Feb	0.269	0.268	0.266	0.264	0.261	0.257	0.253	0.248	0.243	0.236	0.228
Mar	0.269	0.269	0.269	0.269	0.269	0.269	0.268	0.268	0.268	0.267	0.266
Apr	0.269	0.270	0.272	0.275	0.278	0.282	0.286	0.291	0.297	0.303	0.310
May	0.271	0.273	0.276	0.281	0.287	0.294	0.303	0.312	0.322	0.334	0.346
Jun	0.274	0.280	0.285	0.291	0.298	0.307	0.316	0.328	0.341	0.355	0.371
Jul	0.275	0.281	0.287	0.293	0.299	0.305	0.313	0.321	0.330	0.341	0.354
Aug	0.274	0.278	0.282	0.287	0.291	0.295	0.300	0.304	0.309	0.315	0.322
Sep	0.271	0.277	0.280	0.281	0.281	0.281	0.281	0.281	0.281	0.281	0.281
Oct	0.270	0.269	0.268	0.267	0.264	0.261	0.258	0.254	0.250	0.245	0.240
Nov	0.269	0.267	0.264	0.260	0.254	0.247	0.240	0.231	0.222	0.211	0.200
Dec	0.268	0.266	0.262	0.257	0.250	0.242	0.232	0.221	0.209	0.195	0.180

Penman Method with Correction Factor

The original Penman method (Penman 1948) is one of the most theoretically based approaches for estimating PET because it is based on incoming solar energy (i.e., radiation) and aerodynamic characteristics (e.g., wind and humidity). The relative importance of each term varies with climatic conditions. Doorenbos and Pruitt (1977) note that under calm weather conditions the aerodynamic term is usually less important than the energy term, and the results appear to predict evapotranspiration rather closely. They continue to note that under windy conditions and particularly in the more arid regions, the aerodynamic term becomes more important; thus, errors may result in predicting PET. Israelsen and Hansen (1962) appear to concur with Doorenbos and Pruitt (1977) by noting that the coefficients used in the Penman equation:

> " . . . were determined for a rather humid area not far from the ocean and essentially covered with growing vegetation. Experience indicates that the Penman formula applies better under these conditions than in arid, low-humidity areas where temperature and radiant energy may not be as nearly balanced as . . . (in a humid area near the ocean)." (pp. 244-245)

Doorenbos and Pruitt (1977) developed the modified version of the Penman method, called the Penman method with correction factor. It differs from the Penman method by using a revised wind function term in its formulation. The Penman method with correction factor is based on climatic parameters such as maximum, minimum, and mean relative humidity; ratio of actual to maximum possible sunshine hours; average wind speed; average air temperature; saturation and actual vapor pressures; and net shortwave and longwave solar radiation parameters. The governing PET rate equation in the method is as follows:

$$E_{pj} = \begin{cases} c_j\left[f_{wj}\,R_{nj} + (1 - f_{wj})\,f(\overline{U}_j)\,(e_{sj} - e_{aj})\right] & \text{for } T_{aj} > 0^\circ\text{C} \\ 0 & \text{for } T_{aj} \leq 0^\circ\text{C} \end{cases} \tag{5.8}$$

where c_j is the correction factor for the Penman method with correction factor for the *j*-th month (unitless)

f_{wj} is the temperature-related weighting factor for the *j*-th month (unitless)

R_{nj} is the net radiation, in equivalent evaporation, for the *j*-th month (mm d^{-1})

$f(\overline{U}_j)$ is a wind-related function, explained below

e_{aj} is the mean actual vapor pressure of the air for the *j*-th month (mbar)

e_{sj} is the saturation vapor pressure at mean air temperature for the *j*-th month (mbar).

Values for the saturation vapor pressure (e_{sj}) are given in Table 5.3. The following equation, proposed by Bosen (1960) and reported by Linsley et al. (1975), is used in the module to estimate the saturation vapor pressure.

$$e_{sj} \approx 33.8639\left[(0.00738\,T_{aj} + 0.8072)^8 - 0.000019\,|1.8\,T_{aj} + 48| + 0.001316\right] \tag{5.9}$$

(where $|\bullet|$ denotes the absolute value of •.)

Linsley et al. (1975) note that this equation "yields values of saturation vapor pressure over water that are approximated to within one percent in the range of -50 to +55°C (-58 to +131°F)." Because relative humidity is the percent ratio of the actual vapor pressure to the saturation vapor pressure, the maximum and minimum relative humidities obtained from the LCD are used to find the actual vapor pressure (e_{aj}) as follows:

$$e_{aj} = e_{sj}\,\frac{h^{rel}_{avg(j)}}{100} = e_{sj}\,\frac{h^{rel}_{max(j)} - h^{rel}_{min(j)}}{2 \cdot 100} \tag{5.10}$$

where $h^{rel}_{ave(j)}$ is the average percent relative humidity for the *j*-th month (unitless) and

$h^{rel}_{max(j)}$ is the maximum percent relative humidity for the *j*-th month (unitless).

The temperature-related weighting factor (f_{wj}) is a function of altitude as well as temperature. The value for f_{wj} can be obtained from Table 5.4. The wind-related function is defined in the Penman method with correction factor as

$$f(\overline{U}_j) = 0.27\left(1 + f_{hj} \cdot \overline{U}_j \cdot \frac{86.4}{100}\right) \tag{5.11}$$

where 86.4 = factor to convert wind speed from m s^{-1} to km d^{-1}.

Table 5.3. Saturated Vapor Pressure Versus Temperature (after Linsley et al. 1975; Doorenbos and Pruitt 1977)

Temperature (°C)	Vapor Pressure (mbar)	Temperature (°C)	Vapor Pressure (mbar)
0	6.1	24	29.8
1	6.6	25	31.7
2	7.1	26	33.6
3	7.6	27	35.7
4	8.1	28	37.8
5	8.7	29	40.1
6	9.3	30	42.4
7	10.0	31	44.9
8	10.7	32	47.6
9	11.5	33	50.3
10	12.3	34	53.2
11	13.1	35	56.2
12	14.0	36	59.4
13	15.0	37	62.8
14	16.1	38	66.3
15	17.0	39	69.9
16	18.2	40	73.8
17	19.4	50	123.4
18	20.6	60	199.3
19	22.0	70	311.7
20	23.4	80	473.7
21	24.9	90	701.1
22	26.4	100	1013.3
23	28.1		

Table 5.4. Values of Weighting Factor (f_{wj}) for the Effect of Radiation on PET rate at Different Temperatures and Altitudes (after Doorenbos and Pruitt 1977).

	Temperature(°C)																			
Altitude (m)	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
0	0.43	0.46	0.49	0.52	0.55	0.58	0.61	0.64	0.66	0.69	0.71	0.73	0.75	0.77	0.78	0.80	0.82	0.83	0.84	0.85
500	0.44	0.48	.051	0.54	0.57	0.60	0.62	0.65	0.67	0.70	0.72	0.74	0.76	0.78	0.79	0.81	0.82	0.84	0.85	0.86
1000	0.46	0.49	0.52	0.55	0.58	0.61	0.64	0.66	0.69	0.71	0.73	0.75	0.77	0.79	0.80	0.82	0.83	0.85	0.86	0.87
2000	0.49	0.52	0.55	0.58	0.61	0.64	0.66	0.69	0.71	0.73	0.75	0.77	0.79	0.81	0.82	0.84	0.85	0.86	0.87	0.88
3000	0.52	0.55	0.58	0.61	0.64	0.66	0.69	0.71	0.73	0.75	0.77	0.79	0.81	0.82	0.84	0.85	0.86	0.87	0.88	0.89
4000	0.54	0.58	0.61	0.64	0.66	0.69	0.71	0.73	0.75	0.77	0.79	0.81	0.82	0.84	0.85	0.86	0.87	0.89	0.90	0.90

The total net radiation (R_{nj}) is equal to the difference between the net shortwave radiation (R_{nsj}) and the net longwave radiation (R_{nlj}). When converted to heat, R_{nj} can be related to the energy (i.e., extraterrestrial radiation [R_{aj}]) required to evaporate water from an open surface (Doorenbos and Pruitt 1977). To calculate R_{nj}, the following steps are involved:

- Determine R_{aj} using Table 5.5 based on latitude (provided in the LCD) and month of year.

Table 5.5. Extraterrestrial Radiation (R_{aj}) for the Northern Hemisphere Expressed in Equivalent Evaporation (mm d^{-1}) (after Doorenbos and Pruitt 1977)

Latitude	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
50°	3.8	6.1	9.4	12.7	15.8	17.1	16.4	14.1	10.9	7.4	4.5	3.2
48	4.3	6.6	9.8	13.0	15.9	17.2	16.5	14.3	11.2	7.8	5.0	3.7
46	4.9	7.1	10.2	13.3	16.0	17.2	16.6	14.5	11.5	8.3	5.5	4.3
44	5.3	7.6	10.6	13.7	16.1	17.2	16.6	14.7	11.9	8.7	6.0	4.7
42	5.9	8.1	11.0	14.0	16.2	17.3	16.7	15.0	12.2	9.1	6.5	5.2
40	6.4	8.6	11.4	14.3	16.4	17.3	16.7	15.2	12.5	9.6	7.0	5.7
38	6.9	9.0	11.8	14.5	16.4	17.2	16.7	15.3	12.8	10.0	7.5	6.1
36	7.4	9.4	12.1	14.7	16.4	17.2	16.7	15.4	13.1	10.6	8.0	6.6
34	7.9	9.8	12.4	14.8	16.5	17.1	16.8	15.5	13.4	10.8	8.5	7.2
32	8.3	10.2	12.8	15.0	16.5	17.0	16.8	15.6	13.6	11.2	9.0	7.8
30	8.8	10.7	13.1	15.2	16.5	17.0	16.8	15.7	13.9	11.6	9.5	8.3
28	9.3	11.1	13.4	15.3	16.5	16.8	16.7	15.7	14.1	12.0	9.9	8.8
26	9.8	11.5	13.7	15.3	16.4	16.7	16.6	15.7	14.3	12.3	10.3	9.3
24	10.2	11.9	13.9	15.4	16.4	16.6	16.5	15.8	14.5	12.6	10.7	9.7
22	10.7	12.3	14.2	15.5	16.3	16.4	16.4	15.8	14.6	13.0	11.1	10.2
20	11.2	12.7	14.4	15.6	16.3	16.4	16.3	15.9	14.8	13.3	11.6	10.7
18	11.6	13.0	14.6	15.6	16.1	16.1	16.1	15.8	14.9	13.6	12.0	11.1
16	12.0	13.3	14.7	15.6	16.0	15.9	15.9	15.7	15.0	13.9	12.4	11.6
14	12.4	13.6	14.9	15.7	15.8	15.7	15.7	15.7	15.1	14.1	12.8	12.0
12	12.8	13.9	15.1	15.7	15.7	15.5	15.5	15.6	15.2	14.4	13.3	12.5
10	13.2	14.2	15.3	15.7	15.5	15.3	15.3	15.5	15.3	14.7	13.6	12.9
8	13.6	14.5	15.3	15.6	15.3	15.0	15.1	15.4	15.3	14.8	13.9	13.3
6	13.9	14.8	15.4	15.4	15.1	14.7	14.9	15.2	15.3	15.0	14.2	13.7
4	14.3	15.0	15.5	15.5	14.9	14.4	14.6	15.1	15.3	15.1	14.5	14.1
2	14.7	15.3	15.6	15.3	14.6	14.2	14.3	14.9	15.3	15.3	14.8	14.4
0	15.0	15.5	15.7	15.3	14.4	13.9	14.1	14.8	15.3	15.4	15.1	14.8

- Compute the solar radiation (R_{sj}) by correcting R_{aj} for the ratio of the actual to the maximum possible sunshine hours ($r_{sun(j)}$, percentage of possible sunshine in the LCD, or estimated from Equation 5.5).

$$R_{sj} = R_{aj}\left[0.25 + 0.50\, r_{sun(j)}\right] \tag{5.12}$$

where R_{sj} is the solar radiation, in equivalent evaporation, for the *j*-th month (mm d^{-1})
R_{aj} is the extraterrestrial radiation, in equivalent evaporation for the j-th month (mm d^{-1}).

- Compute R_{nsj} by correcting R_{sj} for the reflectiveness of the land surface (Doorenbos and Pruitt 1977):

$$R_{nsj} = R_{sj}(1 - \alpha) \tag{5.13}$$

where R_{nsj} is the net shortwave radiation, in equivalent evaporation, for the *j*-th month (mm d^{-1})
α is the land surface reflectiveness correction parameter (unitless=0.25).

- R_{nlj} is estimated based on the average temperature, the actual vapor pressure (e_{aj}), and the ratio of actual to maximum possible sunshine hours $r_{sun(j)}$ as follows:

$$R_{nlj} = \sigma\left(T_{aj} + 273.15\right)^4\left[0.34 - 0.044\left(e_{aj}\right)^{0.5}\right]\left[0.1 + 0.9\, r_{sun(j)}\right] \tag{5.14}$$

where R_{nlj} is the net longwave radiation, in equivalent evaporation, for the *j*-th month (mm d^{-1})
σ is a constant in the estimation equation for R_{nlj} (unitless=2.0×10^{-9})
273.15 = unit conversion from °C to K.

- Compute R_{nj} as the algebraic difference between R_{nsj} and R_{nlj}:

$$R_{nj} = R_{nsj} - R_{nlj} \tag{5.15}$$

The correction factor (c_j) which compensates for the effects of day and night weather conditions, can be estimated from $h^{rel}_{max(j)}$, R_{sj}, and $\overline{U}_j$. By assuming that the ratio of the daytime to nighttime average wind speeds is equal to 2 (see Section 5.1.3.1), the factor c_j can be estimated from Table 5.6.

Table 5.6. Adjustment Factor (c_j) in the Penman Method with Correction Factor Equation (After Doorenbos and Pruitt 1977)

R_{sj} (mm/d) U_j (m/s)	$h^{rel}_{max(j)} = 30\%$				$h^{rel}_{max(j)} = 60\%$				$h^{rel}_{max(j)} = 90\%$			
	3	6	9	12	3	6	9	12	3	6	9	12
0	0.86	0.90	1.00	1.00	0.96	0.98	1.05	1.05	1.02	1.06	1.10	1.10
3	0.69	0.76	0.85	0.92	0.83	0.91	0.99	1.05	0.89	0.98	1.10	1.14
6	0.53	0.61	0.74	0.84	0.70	0.80	0.94	1.02	0.79	0.92	1.05	1.12
9	0.37	0.48	0.65	0.76	0.59	0.70	0.84	0.95	0.71	0.81	0.96	1.06

5.1.4 Adjusted Precipitation

The average monthly precipitation contained in the LCD is assumed to be rainfall if the adjusted average monthly temperature is above freezing, and snowfall if the temperature is below freezing. This assumption is not completely accurate, because rainfall and snowfall frequently occur during the same month, especially during the springtime. However, if the average temperature for the month is above freezing, much of the snowfall will melt and represent a source of water for percolation and overland runoff.

The assumption used in this methodology is that snow is stored on the ground when the adjusted average temperature is less than or equal to 0°C (32°F). When the temperature rises above freezing, the snow melts and is available for percolation and runoff. Simple empirical relationships are used to estimate snowmelt. Heat necessary to induce snowmelt is derived from radiation, condensation of vapor, convection, air and ground conduction, and rainfall. The four most important sources are vapor condensation, convection, radiation, and rainfall. Of these sources, vapor condensation is considered one of the most important factors, while rainfall ranks fourth as an important heat source (Linsley and Franzini 1972; Linsley et al. 1975; Viessman et al. 1977). Each of these four sources is discussed below.

Vapor Condensation

Viessman et al. (1977) note that heat given off by condensing water vapor in a snowpack is often the most important source of heat for snowmelt. A water vapor supply at the snow surface is formed by the turbulent exchange process. Consequently, a mass transfer equation similar to those presented for evaporation studies fits the melt process (Viessman et al. 1977). An expression for a 6-hr depth of snowmelt is given as (Light 1941 as reported by Viessman et al. 1977)

$$d_{6vc} = \begin{cases} K_1 U_{6,15} (e_a - 6.11) & \text{for } T_6 > 0°C \\ 0 & \text{for } T_6 \le 0°C \end{cases} \tag{5.16}$$

where d_{6vc} is the 6-hr snowmelt from vapor condensation (cm)

K_1 is the theoretical constant in equation for snowmelt by vapor condensation (cm s mbar^{-1} m^{-1})

$U_{6,15}$ is the average 6-hr wind velocity measured at 15 m (50 ft) above the ground (m s^{-1})

e_a is the actual vapor pressure of the air (mbar).

The value of K_1 reportedly varies from 0.01818 to 0.03284 (cm s mbar^{-1} m^{-1}) [0.00320 to 0.00578 (hr in. mbar^{-1} mi^{-1})] (Light 1941 and Wilson 1941, as reported by Viessman et al. 1977). An average value of 0.02557 (cm s mbar^{-1} m^{-1}) [0.0045 (hr in. mbar^{-1} mi^{-1})] is chosen for K_1. If the wind speed measurements were not made at 15 m (50 ft), then they can be calculated as follows

$$U_{6,15} \approx \left(\frac{15}{h_{in}}\right)^{0.17} \overline{U} \tag{5.17}$$

where $\overline{U}$ is the average wind speed (m s^{-1}).

Because available data are on a monthly basis, it is assumed that the 6-hr snowmelt computations can be extended over the month by using adjusted averaged monthly temperatures and wind speeds. By assuming that no evaporation of snow occurs, the monthly estimate of depth of snowmelt from vapor condensation can be expressed as follows:

$$d_{vcj} = \begin{cases} 0.102\, n_{dj} \left(\frac{15}{h_{in}}\right)^{0.17} \overline{U}_j (e_{aj} - 6.11) & \text{for } T_{aj} > 0°C \\ 0 & \text{for } T_{aj} \leq 0°C \end{cases} \tag{5.18}$$

where d_{vcj} is the average monthly snowmelt from vapor condensation for the *j*-th month (cm)

n_{dj} is the number of days in the *j*-th month (unitless).

The actual vapor pressure (e_{aj}) is estimated using Equations 5.9 and 5.10 of Section 5.1.3.2.

Convection

Heat is transferred from the atmosphere to the snowpack by convection (Viessman et al. 1977). The amount of snowmelt by this process is related to temperature and wind speed. Wilson (1941) and Light (1941), as reported by Viessman et al. (1977), provide an expression for estimating the 6-hr depth of snowmelt by convection as

$$d_{6c} = \begin{cases} K_2 U_{6,15}\, T_6 & \text{for } T_6 > 0°C \\ 0 & \text{for } T_6 \leq 0°C \end{cases} \tag{5.19}$$

in which

$$K_2 = 10^{(-1.725 - 5.12\times10^{-5} h_1)} \tag{5.20}$$

where d_{6c} is the 6-hr snowmelt from convection (cm)
K_2 is the heat exchange coefficient as a function of elevation (cm s m^{-1} $^\circ C^{-1}$)
T_6 is the average 6-hr temperature (°C).

It is assumed that the 6-hr snowmelt can be extended over the month by using adjusted averaged monthly temperatures and wind speeds. The monthly estimate for snowmelt from convection is given by

$$d_{cj} = \begin{cases} 4\, n_{dj} K_2 \left(\dfrac{15}{h_{in}}\right)^{0.17} \overline{U}_j T_{aj} & \text{for } T_{aj} > 0^\circ C \\ 0 & \text{for } T_{aj} \le 0^\circ C \end{cases} \tag{5.21}$$

where d_{cj} is the average monthly snowmelt from convection for the *j*-th month (cm).

Radiation

The net amount of shortwave and longwave radiation received by a snowpack can be a very important source of heat energy for snowmelt (Viessman et al. 1977). Viessman et al. (1977) note that, under clear skies, the most significant variables in snowmelt due to radiation are insolation, albedo of snow, and air temperature. The U.S. Army Corps of Engineers (COE 1956) show that cloud cover and height can significantly affect snowmelt from radiation. An approximate method of estimating 12-hr depth of snowmelt from direct solar radiation is given by Wilson (1941). The relationship is of the following form:

$$d_{12rd} = \begin{cases} K_{rd}(1 - 0.75\, c_{sky}) & \text{for } T_{12} > 0^\circ C \\ 0 & \text{for } T_{12} \le 0^\circ C \end{cases} \tag{5.22}$$

where d_{12rd} is the 12-hr snowmelt from radiation (cm)
K_{rd} is the snowmelt occurring by radiation in a half-day in clear weather (cm)
c_{sky} is the mean sky cover for a 12-hr period (tenths) (unitless)
T_{12} is the average 12-hr temperature (°C).

It is assumed that the 12-hr snowmelt can be extended over the month by using monthly averaged degree of cloudiness. The monthly estimate of snowmelt from radiation is given by

$$d_{rdj} = \begin{cases} n_{dj} K_{rdj} (1 - 0.75\, c_{sky(j)}) & \text{for } T_{aj} > 0°C \\ 0 & \text{for } T_{aj} \leq 0°C \end{cases} \tag{5.23}$$

where d_{rdj} is the average monthly snowmelt from radiation for the *j*-th month (cm)

K_{rdj} is the average snowmelt occurring by radiation in a half-day in clear weather for the *j*-th month (cm).

Viessman et al. (1977) provide estimates of the parameter K_{rdj} as a function of month (Table 5.7).

Table 5.7. Half-Day Snowmelt During Clear Weather as a Function of Month (after Viessman et al. 1977)

j	**Month**	**K_{rdj} (cm)**
3	March	0.89
4	April	1.07
5	May	1.22
6	June	1.33

Rainfall

Viessman et al. (1977) note that since the temperature of rain falling on a snowpack is probably low, the heat derived from rainfall is generally small. At higher temperatures, rainfall may constitute a significant heat source; it affects the aging process of the snow, frequently to a great degree. Based on Viessman et al. (1977) and COE (1960), daily depth of snowmelt by rainfall can be estimated by

$$d_{24m} = \begin{cases} 0.032\, d_{pr} T_{24} & \text{for } T_{24} > 0°C \\ 0 & \text{for } T_{24} \leq 0°C \end{cases} \tag{5.24}$$

where d_{24m} is the daily snowmelt during a rainfall event (cm)

d_{pr} is the daily precipitation depth (cm)

T_{24} is the average daily air temperature (°C).

This equation is applied to the an entire month by assuming that the equation is applicable to each rainfall event during the month, and that the air temperature during each event is the same as the adjusted average monthly temperature. Computing the depth of snowmelt from rainfall for each precipitation event in the *j*-th month and summing the results gives the following expression:

$$d_{mj} = \begin{cases} 0.032\, d_{praj}\, T_{aj} & \text{for } T_{aj} > 0°C \\ 0 & \text{for } T_{aj} \leq 0°C \end{cases} \tag{5.25}$$

where d_{mj} is the snowmelt from rainfall for the *j*-th month (cm)
d_{praj} is the precipitation adjusted for snowmelt for the *j*-th month (cm).

Total Monthly Snowmelt

The total depth of snowmelt on a monthly basis is the sum of the snowmelt depths due to vapor condensation, convection, radiation, and rainfall:

$$d_{sj} = \begin{cases} d_{vcj} + d_{cj} + d_{rdj} + d_{mj} & \text{for } T_{aj} > 0°C \\ 0 & \text{for } T_{aj} \leq 0°C \end{cases} \tag{5.26}$$

where d_{sj} is the total snowmelt for the *j*-th month (cm).

The depth of snowmelt is limited by the amount of snow stored on the land surface. When a month has an adjusted monthly temperature greater than freezing and there is snow stored on the land surface, the monthly precipitation volume is adjusted to account for snowmelt as follows:

$$d_{praj} = d_{pruj} + d_{sj} \tag{5.27}$$

where d_{pruj} is the unadjusted precipitation depth for the *j*-th month obtained from the LCD (cm).

The adjusted precipitation (d_{praj}) is used to compute net overland runoff and deep-drainage percolation.

5.1.5 Overland Runoff

Overland runoff is computed using the SCS Curve Number technique (SCS 1972, 1982; Kent 1973; USBR 1977). The factors considered in this method include surface soil characteristics, vegetative cover, land use, antecedent moisture conditions, and geographic locale. To apply this technique in the module, the following is assumed:

1. The monthly precipitation depth can be equally distributed among the total number of recorded precipitation events.

2. The number of precipitation events per month can be defined as the mean number of days with at least 0.254 mm (0.01 in.) of precipitation (as listed in the LCD).

3. There is no overland runoff when the adjusted average monthly temperature is equal to or below freezing (because precipitation is assumed to be stored on the land surface in the form of snow).

4. The method is applicable, although snow may be covering the land surface. This condition rarely occurs, because most snow is usually melted in the first month that the average temperature rises above freezing.

Using the SCS Curve Number technique, the total monthly runoff from the waste site is estimated as follows:

$$d_{roj} = \begin{cases} \dfrac{\{d_{praj}\, n_{scs} - 0.508\, n_{pj}\,[1000 - 10\, n_{scs}]\}^2}{n_{scs}\, m_j \{d_{praj}\, n_{scs} - 2.032\, n_{pj}\,[1000 - 10\, n_{scs}]\}} & \text{for } T_{aj} > 0°\text{C and } d_{praj}\, n_{scs} > 0.508\, n_{pj}\,[1000 - 10\, n_{scs}] \\ 0 & \text{for } T_{aj} \le 0°\text{C or } d_{praj}\, n_{scs} \le 0.508\, n_{pj}\,[1000 - 10\, n_{scs}] \end{cases} \tag{5.28}$$

where d_{roj} is the overland runoff for the j-th month (cm)
n_{scs} is the SCS Curve Number used for runoff calculations (unitless)
n_{pj} is the number of precipitation events during the j-th month (unitless).

A complete discussion reviewing the development of Equation 5.28 is presented in Whelan et al. (1987).

5.1.6 Maximum and Potential Percolation

The maximum amount of moisture available for percolation (i.e., maximum percolation) is the adjusted precipitation less overland runoff:

$$I_{max(j)} = \begin{cases} d_{praj} - d_{roj} & \text{for } T_{aj} > 0°\text{C} \\ 0 & \text{for } T_{aj} \le 0°\text{C} \end{cases} \tag{5.29}$$

where $I_{max(j)}$ is the maximum amount of moisture available for percolation in the j-th month (cm).

Potential percolation is the maximum percolation ($I_{max(j)}$) less PET. Therefore, the maximum percolation is first used to satisfy the demands of PET before soil moisture recharge or deep-drainage percolation can occur. Potential percolation is expressed as follows:

$$I_{pot(j)} = \begin{cases} I_{max(j)} - \dfrac{n_{dj}\, E_{pj}}{10} & \text{for } T_{aj} > 0°\text{C} \\ 0 & \text{for } T_{aj} \le 0°\text{C} \end{cases} \tag{5.30}$$

where $I_{pot(j)}$ is the potential percolation for the *j*-th month (cm)
E_{pj} is the potential evapotranspiration rate for the *j*-th month (mm d^{-1}).

The factor $(n_{dj}/10)$ in Equation 5.30 is needed to convert PET rate (mm d^{-1}) to PET (cm). Note that potential percolation is positive during wet seasons and negative during dry seasons.

5.1.7 Accumulated Potential Water Loss and Soil Moisture Storage

Accumulated potential water loss and soil moisture storage are computed using the methodology outlined by Thornthwaite and Mather (1955, 1957). Accumulated potential water loss is the potential deficiency of soil moisture associated with moisture contents below the water-holding capacity of a soil. Thus, for each soil moisture content there is an associated accumulated potential water loss. Accumulated potential water loss is 1) increased during dry seasons because of an insufficient supply of water (i.e., maximum percolation) to meet the demands of PET, 2) reduced during wet seasons due to the recharge of soil moisture, and 3) equals zero when soil moisture storage equals the water-holding capacity of the soil.

Accumulated potential water loss is never equal to the actual water loss, because as the soil moisture declines during a dry season, it becomes increasingly difficult to extract additional water from the soil. This causes AET to be less than PET during the dry season. The relationship between accumulated potential water loss and soil moisture is given in Thornthwaite and Mather (1957) as a set of soil moisture retention tables. These tables are used by the module to compute soil moisture storage for dry months given an accumulated potential water loss, and to compute the accumulated potential water loss for wet months given a moisture content. An example soil moisture retention table is shown in Table 5.8.

The accumulated potential water loss for a given month of the dry season is the sum of the absolute value of potential percolation for that month and the accumulated potential water loss of the previous month. This new accumulated potential water loss is then used to calculate soil moisture for the given month. For any given month of the wet season, soil moisture is calculated as the sum of the potential percolation for that month and the soil moisture of the previous month.

Table 5.8. Example Soil Moisture Retention Table for 150-mm Water-Holding Capacity of the Root Zone (after Thornthwaite and Mather 1957)(a)

	Soil Moisture Storage ($S_{m(j)}$)									
$-w_{pj}$ → ↓	0	1	2	3	4	5	6	7	8	9
10	140	139	138	137	136	135	134	133	132	131
20	131	130	129	128	127	127	126	125	124	123
30	122	122	121	120	119	118	117	116	115	114
40	114	113	113	112	111	111	110	109	108	107
50	107	106	106	105	104	103	103	102	101	100
60	100	99	98	97	97	97	96	95	94	93
70	93	92	92	91	90	90	89	89	88	87
80	87	86	86	85	84	84	84	83	83	82
90	82	81	81	80	79	79	78	77	77	76
100	76	76	75	75	74	74	73	73	72	71
110	71	71	70	70	69	69	68	68	67	67
120	66	66	66	65	65	64	64	63	63	62
130	62	62	61	61	60	60	60	59	59	58
140	58	58	57	57	56	56	55	55	54	54
150	54	53	53	53	52	52	52	52	51	51
160	51	51	50	50	50	49	49	48	48	47
170	47	47	47	46	46	46	45	45	45	44
180	44	44	44	43	43	43	42	42	42	41
190	41	41	41	40	40	40	40	39	39	39
200	39	38	38	38	37	37	37	37	36	36
210	36	36	35	35	35	35	35	34	34	34
220	34	34	33	33	33	33	33	32	32	32
230	32	31	31	31	31	31	30	30	30	30
240	30	29	29	29	29	29	28	28	28	28
250	28	27	27	27	27	27	26	26	26	26
260	26	26	25	25	25	25	25	24	24	24
270	24	24	24	23	23	23	23	23	23	23
280	22	22	22	22	22	22	22	22	21	21

Table 5.8. (contd)

	Soil Moisture Storage ($S_{m(j)}$)									
$-W_{pj}$ → ↓	0	1	2	3	4	5	6	7	8	9
290	21	21	21	20	20	20	20	20	20	20
300	20	19	19	19	19	19	19	19	18	18
310	18	18	18	18	18	18	18	17	17	17
320	17	17	17	17	17	17	17	16	16	16
330	16	16	16	16	16	16	16	15	15	15
340	15	15	15	15	15	15	14	14	14	14
350	14	14	14	14	14	14	14	13	13	13
360	13	13	13	13	13	13	13	12	12	12
370	12	12	12	12	12	12	12	12	11	11
380	11	11	11	11	11	11	11	11	11	11
390	11	11	11	10	10	10	10	10	10	10
400	10	10	10	10	10	10	10	10	9	9
410	9	9	9	9	9	9	9	9	9	9
420	9	9	9	8	8	8	8	8	8	8
430	8	8	8	8	8	8	8	8	8	8
440	8	8	8	7	7	7	7	7	7	7

(a) Soil moisture retained after different amounts of potential evapotranspiration have occurred. Water-holding capacity of the soil root zone is 150 mm.

If the soil moisture exceeds the water-holding capacity, the soil moisture is set equal to the water-holding capacity:

$$S_{m(j)} = \begin{cases} S_{m(j-1)} + I_{pot(j)} & \text{for } S_{m(j-1)} + I_{pot(j)} < w_{WHC} \\ w_{WHC} & \text{for } S_{m(j-1)} + I_{pot(j)} \geq w_{WHC} \end{cases} \tag{5.31}$$

where $S_{m(j)}$ is the soil moisture storage for the *j*-th month (cm)
w_{WHC} is the water-holding capacity of the soil (c).

If the soil moisture remains below the water-holding capacity, a new accumulated potential water loss is computed using the soil moisture retention tables. The change in the soil moisture storage is the difference between the current and previous month's soil moisture storage:

$$\Delta S_{m(j)} = S_{m(j)} - S_{m(j-1)} \tag{5.32}$$

Thus, the change in soil moisture is positive if the soil moisture has increased, and negative if the soil moisture has decreased.

Wet seasons are referred to as adequate or inadequate. An adequate wet season is one with sufficient potential percolation to fully replace the soil moisture depleted during the previous dry season. When this is the case, the computation of monthly soil moisture and accumulated potential water loss values is simple. For the last month of an adequate wet season, the soil moisture is equal to the water-holding capacity of the soil and accumulated potential water loss is zero. Then, starting with the first month of the following dry season, soil moisture and accumulated potential water loss are computed as described in the previous paragraph for all the remaining months of the year.

An inadequate wet season is one without sufficient potential percolation to fully replace the soil moisture depleted during the previous dry season. When this is the case, the computation of monthly soil moisture and accumulated potential water loss values is more complicated. Thornthwaite and Mather (1957) describe a method of successive approximations to determine a starting value of accumulated potential water loss from which to start the monthly computations. This involves 1) estimating the potential water deficiency at the end of the wet season, 2) estimating the accumulated potential water loss at the end of the dry season by adding on all the negative potential percolation values, 3) determining the associated soil moisture using the soil moisture retention tables, 4) adding on the positive potential percolation values for the wet season to estimate the soil moisture at the end of the wet season, 5) converting that soil moisture back to accumulated potential water loss, and then repeating the process until convergence is achieved. This process can become quite complicated if a site contains multiple wet and dry seasons. Details of the aforementioned calculations of accumulated potential water loss and soil moisture storage are given in Whelan et al. (1987).

A variation on this approach is used in the source term release module. Soil moisture is initially assumed to be at the water-holding capacity of the soil in January, and the accumulated potential water loss is zero. Then, soil moisture and accumulated potential water loss are computed for each month in sequence, year after year, until the values in successive years for January converge. When this occurs, the soil moisture and accumulated potential water loss for each month will have converged. The benefit of this approach is that it will work for any number of wet and dry seasons, regardless of whether the wet seasons are adequate or inadequate.

5.1.8 Actual Evapotranspiration

Actual evapotranspiration equals PET during the wet season (i.e., during months where potential percolation is greater than zero). During the dry season, AET is the sum of maximum percolation (i.e., precipitation less overland runoff) and the amount of moisture withdrawn from storage (i.e., the negative of the change in soil moisture storage):

$$E_{aj} = \begin{cases} \dfrac{n_{aj} E_{pj}}{10} & \text{for } I_{pot(j)} \geq 0 \text{ (wet season)} \\ I_{max(j)} - \Delta S_{m(j)} & \text{for } I_{pot(j)} < 0 \text{ (dry season)} \end{cases} \tag{5.33}$$

where E_{aj} is the actual evapotranspiration for the *j*-th month (cm).

5.1.9 Infiltration Generation

The leachate generated in any month is the amount of maximum percolation in excess of AET and soil moisture recharge. If all the maximum percolation in a given month is used for AET and soil moisture recharge, or if the adjusted temperature for the month is equal to or below freezing, then no leachate is generated:

$$I_j = \begin{cases} I_{max(j)} - E_{aj} - \Delta S_{m(j)} & \text{for } T_{aj} > 0°C \\ 0 & \text{for } T_{aj} \leq 0°C \end{cases} \tag{5.34}$$

where I_j is the leachate generation for the *j*-th month (cm).

The module then calculates an annual infiltration rate (i.e. Darcy flux density) by summing the monthly values of leaching

$$q_w = \frac{\sum_{j=1}^{12} I_j}{(1 \text{ yr})} \tag{5.35}$$

where j is the index on the month (unitless).

Like natural soil, waste-site material exhibits a certain water-holding capacity. Fenn et al. (1975) note that the amount of water that can be added and stored in the waste material depends on the composition of the waste and its initial moisture content (which can vary widely) when delivered to the site. Theoretically speaking, water movement through a waste layer will act in a similar manner as water movement through a soil layer; the field capacity must be exceeded before leachate movement. Practically speaking, some channeling of water, from the heterogeneities associated with the waste, will occur before the attainment of field capacity.

In an effort to avoid the complex nature of various waste forms, the module assumes that surfacial waste sites act like surfacial natural soil, and that the moisture content of the buried waste sites equals field capacity. Therefore, the moisture that percolates through the bottom of the waste does so at a rate equal to q_w as calculated above.

5.2 Wind Suspension Rate Calculations

This section deals specifically with wind suspension emissions calculations. Volatilization as a release mechanism is discussed in Section 5.4.4.

The release of contaminants into the atmosphere is often a function of local conditions. Important factors can be temperature, moisture, wind speed, surface characteristics (e.g., crust formation, roughness, or vegetation cover), the physical state and chemical form of the contaminant (e.g., gas or particulate, reactive or nonreactive), and location of the contaminant (i.e., on the surface, buried under a soil layer, immobilized by in-situ treatments, or containerized).

5.2.1 Suspension of Surface Particles

Particulate fugitive releases of contaminants are defined as emissions resulting from suspension of exposed surface contamination by wind and mechanical processes to the air. If a site has only buried or immobilized wastes there will be no suspension emissions. If the site has exposed surfaces with contamination or surfaces with contamination are exposed due to the erosion of cover materials, there will be emissions to the atmosphere caused by the suspension of respirable particulates.

A surface cover with contaminants may be the result of either waste storage (e.g., mill tailings) or contamination by the operation of a facility. The latter contamination may occur on natural surfaces (e.g., soil) or artificial surfaces (e.g., concrete pads, roadways). The potential for suspension of contaminants varies greatly because of the wide variety of surface types and activities expected on the surfaces.

The suspension of particles from the surface may occur as the result of wind action (Bagnold 1941; Sehmel and Lloyd 1976) or other physical action on the surface (Sehmel 1976). Atmospheric turbulence plays a role in determining the extent to which the air movement over the surface can suspend surface particles. Local mechanical activity on the surface, such as animal grazing, vehicular traffic, walking, and earth moving can greatly increase the fugitive particulate release rates compared to an undisturbed surface.

The suspension of respirable particles (particles with diameters less than 10 μm) from contaminated areas at U.S. Department of Energy (DOE) sites is calculated using empirical relationships based on studies of wind erosion and surface disruption. The source-term release module outputs for suspension from contaminated surface areas are expressed in terms of an airborne soil concentration normalized to a unit area of contaminated surface. These soil concentration arrays are converted to arrays of contaminant concentrations using the fraction of surface contamination in the suspended soil.

Computing the suspension of contaminants from a surface into the atmosphere requires both contaminant and site data. These data are used to define which formulations, if any, apply to the site. If a computation is appropriate, these data are used to compute the suspension rates.

The source-term release module methodology for computing suspension rates is an adaptation of the methodology proposed by Cowherd et al. (1985) for rapid computation of potential long-term impacts from spills of hazardous materials. This methodology, which includes formulations for contaminant suspension by winds, vehicular traffic, and other physical disturbances of the surface, is similar to, but not identical to, the U.S. Environmental Protection Agency's (EPA) AP-42 revision of the Cowherd et al. (1985) model for industrial wind erosion (EPA 1988b, 1995).

5.2.2 Emission Rate Computation

The wind suspension rate is calculated from the emission rate for respirable particulates

$$S = \frac{E_{wind}}{\beta_s \cdot A} \tag{5.36}$$

where S is the volumetric wind suspension rate (cm yr^{-1})
E_{wind} is the total emission rate for wind erosion (g yr^{-1}).

The total emission rate for wind erosion is the sum of the wind-erosion/mechanical-disturbance and vehicular travel emission rates.

$$E_{wind} = E_{wm} + E_{veh} \tag{5.37}$$

where E_{wm} is the emission rate for wind/mechanical suspension (g yr^{-1})
E_{veh} is the emission rate for suspension due to vehicular travel (g yr^{-1}).

In addition to using the wind suspension rate, S, in the source-term module, the total emission rate, E_{wind}, is used as input to the atmospheric dispersion, transport, and deposition model.

5.2.3 Wind Erosion and Mechanical Suspension

Cowherd et al. (1985) define the steps for determining potential respirable particulate emission from wind erosion. The soil particle size distribution, apparent roughness of the site, vegetation cover, presence of a crust on the soil, and presence of nonerodible elements (e.g., large stones) are used to define the potential for suspension. Depending on the results of their procedure, the site is characterized as having 1) unlimited erosion potential, 2) limited erosion potential, or 3) no erosion potential.

The methodology uses different formulations for the two cases with wind erosion potential. Cowherd et al. (1985) suggest that if the site is completely covered with vegetation or if there is a thick crust (or a wet, saturated soil) and if no mechanical disturbances occur at the site, it can be assumed that no contaminants are suspended. However, for certain contaminants, even very small suspension rates from well-stabilized surfaces may be significant. These wind erosion formulations give results comparable to using resuspension factors over a range of surfaces from bare, unstabilized surfaces to well-stabilized surfaces (Whelan et al. 1989).

In the module, the wind/mechanical emission rate for a surface is computed as the sum of the unlimited and limited erosion emissions. The emission rate terms were not summed in the original methodology described by Cowherd et al. (1985).

$$E_{wm} = E_{lim} + E_{unlim} \tag{5.38}$$

where E_{lim} is the annual average limited emission rate per unit surface area (g yr^{-1})
E_{unlim} is the annual average unlimited emission rate per unit surface area (g yr^{-1}).

Limited Erosion Calculation

The potential for wind erosion is quantified in terms of a threshold friction velocity. The greater the value of the threshold friction velocity for a site, the lower the potential for particle suspension. The threshold friction velocity for the contaminated area is determined by knowing the mode of the aggregate particulate size distribution (which is derived from the soil composition) and using a formula derived from the graphical relationship given by Gillette (1980):

$$U_f = \frac{f_{ne} \exp[0.412 \ln (A_{dist}) + 4.17]}{100} \tag{5.39}$$

where U_f is the threshold friction velocity (m s^{-1})
f_{ne} is the nonerodible elements correction factor (unitless)
A_{dist} is the aggregate size distribution (mm).

The aggregate size distribution is estimated using

$$A_{dist} = 0.0106 P_{sand} + 0.05 \tag{5.40}$$

where P_{sand} is the percent sand (unitless).

From the viewpoint of increasing the potential for suspension, this relationship provides relatively realistic estimates for soils with greater than 75% sand content. For other soils, the relationship provides relatively conservative estimates that are more typical of disturbed soils than undisturbed soils.

The correction factor, f_{ne}, in Equation 5.39 allows for the effects of any non-erodible elements in the contaminated area. This correction factor depends on the fraction of surface coverage and is estimated from graphical results given by Cowherd et al. (1985), derived from wind tunnel studies by Marshall (1971). As the silhouette area of nonerodible elements increases, so does the threshold friction velocity. If the threshold friction velocity is less than 0.75 m s^{-1}, the area has unlimited erosion potential; otherwise, the area has only limited erosion potential.

Once the threshold friction velocity has been determined, the critical wind speed at a given height above the surface can be determined using the equation(a)

$$U_c = \frac{1}{c_{vk}} U_f \ln\left(\frac{h_{ref}}{L_r}\right) \tag{5.41}$$

where	U_c	is the critical wind speed at the reference height above the soil surface (m s^{-1})
	c_{vk}	is the von Karman constant (unitless)
	h_{ref}	is the reference height above the soil surface (m)
	L_r	is the surface roughness length (m).

The critical wind speed is one of the parameters used below to define the erosion potential. The value of h_{ref} recommended by Cowherd et al. (1985) is 7 m. The surface roughness length of the site, L_r, is related to the size and spacing of the roughness elements in the area. The von Karman constant is equal to 0.4.

For estimating particulate emissions from a contaminated area having limited wind-erosion potential, the following equation is used to predict potential emissions:

$$E_{lim} = (8.76\times10^{-4} A)(0.83)\left[\frac{f_d\, E_{pot}\,(1 - f_v)}{\left(\frac{f_{PE}}{50}\right)^2}\right] f_{cr} \tag{5.42}$$

where	f_d	is the frequency of mechanical disturbances ($month^{-1}$)
	E_{pot}	is the erosion potential (g m^{-2})
	f_v	is the vegetation coverage on surface (unitless)
	f_{PE}	is the Thornthwaite's Precipitation-Evaporation (PE) Index (unitless)
	f_{cr}	is the fraction of soil surface that is crusted (unitless).

In Equation 5.42, the factor ($8.76\times10^{-4}A$) is needed to convert E_{lim} from the units used in Cowherd et al. (1985) (mg m^{-2} hr^{-1}) to those used in this report (g yr^{-1}). The frequency of disturbances per month, f_d, is defined as the number of actions that could expose fresh surface material. If the entire area is not disturbed, this frequency should be weighted to reflect the actual area exposed. A disturbance could be vehicular traffic, plowing or turning of the soil, mining, or construction. However, vehicular traffic is accounted for by separate expressions described in the next section. The erosion potential, E_{pot}, depends on the maximum wind speed, U_{max}, so that

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(a) Units for the surface roughness length are listed as meters (m) for consistency with Equation 5.39; the common units for this variable are centimeters (cm).

$$E_{pot} = \begin{cases} 6.7\ (U_{max} - U_c) & \text{if } U_{max} \geq U_c \\ 0 & \text{if } U_{max} < U_c \end{cases} \tag{5.43}$$

where U_{max} is the maximum wind speed at a reference height above the soil surface (m s^{-1}).

The vegetation fraction, f_v, varies from 0 for bare ground to 1 for total coverage. The Thornthwaite's PE Index, f_{PE}, is used as a moisture-correction parameter for wind-generated emissions. Cowherd et al. (1985) provide a map with values of f_{PE} for all regions in the contiguous United States.

Unlimited Erosion Calculation

For unlimited erosion potential, the relationship for the surface emission rate is

$$E_{unlim} = (0.876\ A)(0.036)(1 - f_v)\left(\frac{\overline{U}_y}{U_c}\right)^3 F(U_c,\overline{U}_y)\ (1 - f_{cr}) \tag{5.44}$$

where $\overline{U}_y$ is the mean annual wind speed (m s^{-1})

$F(U_c, \overline{U}_y)$ is a function defined below.

In Equation 5.44, the factor (0.876 A) is needed to convert E_{unlim} from the units used in Cowherd et al. (1985) (g m^{-2} hr^{-1}) to those used in this report (g yr^{-1}).

The vertical flux of particles smaller than 10 μm in diameter is assumed to be proportional to the cube of the horizontal wind speed. This relationship was originally developed from measurements made by O'Brien and Rindlaub (1936) in studies at the mouth of the Columbia River and later measurements made by Bagnold (1941) in the Egyptian desert. Chepil (1951) found this same relationship using results from wind-tunnel experiments.

The function, $F(U_c, \overline{U}_y)$, comes from the cubic relationship of the vertical transport of particles and the wind speed. It is defined in graphical format by Cowherd et al. (1985). This relationship can be broken into the following discrete parts:

$$F(U_c,\overline{U}_y) = \begin{cases} 0.0 & \text{if } x < 0.0 \\ 1.91 & \text{if } 0.0 \le x < 0.5 \\ 1.9-(x-0.5)\ 0.6 & \text{if } 0.5 \le x < 1.0 \\ 1.6-(x-1.0)\ 1.3 & \text{if } 1.0 \le x < 2.0 \\ 0.18x(8x^2+12)e^{-x^2} & \text{if } 2.0 \le x \end{cases} \qquad (5.45)$$

where $x = 0.886(U_c/\ \overline{U}_y)$.

5.2.4 Vehicular Suspension

For suspension of particles due to vehicular traffic on unpaved contaminated surfaces, the emission rate is computed from

$$E_{veh} = 365\ E_{road}\ L_{road}\ n_v \qquad (5.46)$$

where E_{road} is the emission rate from road surfaces (g vehicle^{-1} km^{-1})
L_{road} is the distance of travel over contaminated surface (km)
n_v is the average number of vehicles traveling over the contaminated surface per day (vehicle d^{-1}).

The factor of 365 in Equation 5.46 converts g d^{-1} into g yr^{-1}. The emission rate from road surfaces is simply the combination of suspension from unpaved road surfaces and paved surfaces.

$$E_{road} = E_{unpav} + E_{pav} \qquad (5.47)$$

where E_{unpav} is the emission rate for traffic on unpaved roads (g vehicle^{-1} km^{-1})
E_{pav} is the emission rate for traffic on paved roads (g vehicle^{-1} km^{-1}).

Formulations used to compute pollutant emissions per unit area resulting from the mechanical disturbances by vehicle traffic are also based on Cowherd et al. (1985). The pollutant emission caused by traffic moving over unpaved surfaces is computed using

$$E_{unpav} = (0.85)\left(\frac{P_{silt}}{10}\right)\left(\frac{v_{veh}}{24}\right)^{0.8}\left(\frac{M_{veh}}{7}\right)^{0.3}\left(\frac{n_w}{6}\right)^{1.2}\left(\frac{365\ -\ n_p}{365}\right) \qquad (5.48)$$

where P_{silt} is the percent silt plus very fine sand (unitless)
v_{veh} is the mean vehicle speed (km hr^{-1})
M_{veh} is the mean vehicle weight (Mg)

n_w is the mean number of wheels on a vehicle (unitless)
n_p is the number of days with at least 0.254 mm (0.01 in.) of precipitation per year (unitless).

Site-specific information from local sources is normally obtained for each of the parameters. When site-specific data are not available, the default values given by Cowherd et al. (1985), which are listed in Table 5.9, may be used.

Values for n_p are obtained from a local source of meteorological data. For a paved road, E_{pav} is calculated using Equation 5.48. An additional assumption is made for paved roads; only 1% of the road surface is covered with respirable material.

Table 5.9. Default Values for Independent Variables of Equation 5.48[a,b]

Site	P_{silt} (%)	v_{veh} (km hr^{-1})	M_{veh} (Mg)	n_w (#)
Rural/Residential	15 (5-68)	48 (40-64)	2	4
Industrial	8 (2-29)	24 (8-32)	3 15 26	4 6 10

(a) Based on Cowherd et al. (1985).
(b) Numbers in parentheses are ranges of measured values.

5.3 Water Erosion Rate Calculations

The most widely used method for predicting soil loss from overland areas is the Universal Soil Loss Equation (USLE) (Novotny and Chesters 1981; Overcash and Davidson 1980; Mitchell and Bubenzer 1980). Overcash and Davidson (1980) note that the USLE "is and will continue to be for the foreseeable future, the best equation for estimating long term, average-annual and monthly soil loss." The USLE was developed to predict average-annual soil loss from sheet, rill, and interrill erosion. Sheet erosion refers to sediment movement from small natural areas having little topographic relief (Eagleson 1970). Rill erosion refers to concentrated soil movement due to channelized flow (Meyer 1974). Interrill erosion refers to uniform soil movement in the remaining areas between rills; interrill erosion results primarily from raindrop impact (Meyer 1974).

Wischmeier (1976) notes that the USLE may be used to predict average-annual soil loss from a field-sized plot with specified land use conditions (Mitchell and Bubenzer 1980). The assumptions associated with the USLE are as follows (Goldman el al. 1986; Novotny and Chesters 1981; Foster 1976; Onstad and Foster 1975):

- The USLE is an empirically derived algorithm and does not mathematically represent the actual erosion process.

- The USLE was developed to estimate long-term, average-annual, or seasonal soil loss. Unusual rainfall seasons, especially higher than normal rainfall and atypically heavy storms, may produce more sediment than estimated.

- The USLE estimates soil loss on upland areas only; it does not estimate sediment deposition. Sediment deposition generally occurs at the bottom of a slope (i.e., change in grade) where the slope becomes milder.

- The USLE estimates sheet, rill, and interrill erosion and does not estimate channel or gully erosion. Gully erosion, caused by concentrated flows of water, is not accounted for by the equation and yet can produce large volumes of eroded soil.

- The USLE was developed originally to address soil loss from field-sized plots, although with proper care, watersheds can be addressed.

- Because the USLE only estimates the volume of sediment loss (i.e., the volume of soil detached and transported some distance), it can be used to estimate sediment transport capacity at a site.

- Because the USLE represents an empirically derived expression, consistently accurate estimates of soil loss are fortuitous at best.[a]

- The USLE does not estimate soil loss from single storm events unless a modified form of the original equation is used.

The general form of the USLE, as expressed in metric units, is as follows (Goldman et al. 1986):

$$A_{loss} = R_{fact}\, K_{fact}\, S_{fact}\, C_{fact}\, P_{fact} \tag{5.49}$$

where A_{loss} is the average-annual soil loss (t ha^{-1} yr^{-1})
R_{fact} is the rainfall erosivity factor (100 m) (t ha^{-1}) (cm hr^{-1})
K_{fact} is the soil erodibility factor (t ha^{-1} yr^{-1} per unit R_{fact})
S_{fact} is the slope length and steepness factor (unitless)
C_{fact} is the vegetative cover factor (unitless)
P_{fact} is the erosion control practice factor (unitless).

The five factors are multiplied together to produce an estimate of the soil eroded from the site in an average year. Goldman et al. (1986) note that the USLE is most effective when evaluation of site characteristics is done over areas no larger than 40 ha (100 acre). To produce the most representative results, the soil loss analysis at the waste site should be conducted over areas that have similar conditions.

(a) Although the USLE is best used to evaluate the relative effectiveness of different land use patterns and practices, this does not diminish its utility for predicting soil loss, especially as it relates to the source-term release module methodology.

Generally, the waste sites are small enough such that these criteria are approximately met. At sites where these conditions cannot be approximated, the site can be subdivided into smaller areas. The five factors constituting the USLE are discussed in more detail as follows.

5.3.1 Rainfall Erosivity Factor

The rainfall erosivity factor (R-factor) is based on kinetic energy considerations of falling rain (Whelan 1980) and represents a measure of the erosive force and intensity of rain in a normal year (Goldman et al. 1986). Two components of the factor are the total energy and the maximum 30-min intensity of storms (i.e., the EI factor as defined by Wischmeier and Smith 1978, 1958). The R-factor is the sum of the product of these two components for all major storms in the area during an average year.

Although R-factors have been estimated for the entire United States, they only reflect regional-type conditions; as such, Goldman et al. (1986) note that irregular topography in the western portions of the United States makes use of these regional-type calculations impractical. For the western United States, they suggest basing the R-factor on rainfall data. Wischmeier and Smith (1978) report that results of an investigation at the Runoff and Soil Loss Data Center at Purdue University showed that the R-factor could be approximated with reasonable accuracy by using the 2-year, 6-hr rainfall frequency distribution. Based on this frequency distribution, regression equations were developed to define R-factors for three different storm types (i.e., Type I, Type IA, and Type II).

A Type II storm is characterized by gradually increasing rainfall followed by a strong peak in rainfall intensity that tapers off to low-intensity rain. Type II storms occur in 1) the eastern portions of California (i.e., east of the Sierra Nevada), Washington, and Oregon (Kent 1973; Goldman et al. 1986; Mitchell and Bubenzer 1980); 2) all of Idaho, Montana, Nevada, Utah, Wyoming, Arizona, and New Mexico (Kent 1973; Goldman et al. 1986; Mitchell and Bubenzer 1980); and 3) the remaining portions of the United States not covered by-Type I and Type IA storms (Kent 1973; Mitchell and Bubenzer 1980).

Type I and IA storms occur in the maritime climate. Type I is typical of storms that occur in southern and central western California; these storms have a milder but definite peak similar to that of Type II storms. Type IA storms, which are characteristic of storms in coastal areas of northern California, Oregon, Washington, and the western slopes of the Sierra Nevada, have a low broad peak in the rainfall distribution (Goldman et al. 1986; Mitchell and Bubenzer 1980).

The equations that have been developed for estimating R-factors, based on storm type and rainfall-frequency distribution, are (Mitchell and Bubenzer 1980; Goldman et al. 1986):

$$R_{fact} = \begin{cases} (0.2232)\,(16.55)\,(P_{2,6})^{2.20} & \text{for Type I Storm} \\ (0.2232)\,(10.20)\,(P_{2,6})^{2.20} & \text{for Type IA Storm} \\ (0.2296)\,(27.00)\,(P_{2,6})^{2.17} & \text{for Type II Storm} \end{cases} \tag{5.50}$$

where $P_{2,6}$ is the 2-year recurrence interval, 6-hr duration rainfall depth (cm).

The factors (0.2232) and (0.2296) in Equation 5.50 are needed to convert R_{fact} from the English units used in Goldman et al. (1986) to the metric units used in this report. When the rainfall volume for the 2-year, 6-hr rainfall-frequency distribution and the corresponding R-factors are compared, it is evident that the stronger the peak intensity of the typical storm that is characteristic of a given area, the larger the rainfall erosivity factor.

The R-factor described by Equation 5.50 does not include the erosive forces from thaw or snowmelt. Mitchell and Bubenzer (1980) note that McCool et al. (1974, 1976) show that a major erosion potential occurs in the form of low-intensity rainfall or snow during winter months. Wischmeier and Smith (1978) suggest modifying the R-factor at those sites where snowmelt may be important. To provide more discrimination between those sites that traditionally have snowmelt runoff from those where it occurs occasionally, the average-annual R-factors, as defined by Equation 5.50, are increased by an amount equaling 0.591 times the total precipitation (in cm) associated with those months having an average monthly temperature below freezing, including the first month following the last freezing month.(a)

5.3.2 Soil Erodibility Factor

The soil erodibility factor (K-factor) is a quantitative description of the inherent erodibility of a particular soil; it is a measure of the susceptibility of soil particles to detachment and transport by rainfall and runoff. For a particular soil, the soil erodibility factor is the rate of erosion per unit erosion index from a standard plot. The factor reflects the fact that different soils erode at different rates when the other factors that affect erosion (e.g., infiltration rate, permeability, total water capacity, dispersion, rain splash, and abrasion) are the same. Texture is the principal factor affecting K_{fact}, but structure, organic matter, and permeability also contribute. The soil erodibility factor ranges in value from 0.02 to 0.69 (Goldman et al. 1986; Mitchell and Bubenzer 1980).

Goldman et al. (1986) note that several methods can be used to estimate the K-factor. The most frequently used are 1) SCS County Soil Survey reports compiled for many counties in the United States and 2) nomographs relating K-factors to topsoil conditions. The SCS county soil surveys contain soil maps superimposed on aerial photographs. The maps permit easy location of sites and tentative determination of soil series. Recent surveys list K-factors for the soil series in the table outlining the soil's physical and chemical properties. Goldman et al. (1986) note that this method of determining K-factors should only be used if minimal soil disturbance at the site is anticipated and a site analysis is unavailable.

The preferred method, according to Goldman et al. (1986), for determining K-factors is the nomograph method based on the work by Wischmeier et al. (1971) and is mathematically represented as follows:

(a) Note that Wischmeier and Smith (1978) suggest using the precipitation total for the entire period from December through March. Because the runoff volume associated with the MEPAS methodology is based on historically averaged monthly precipitation amounts, it is difficult to determine a priori which locations will traditionally have significant snowmelt runoff. To provide some differentiation between sites, the monthly average temperature is used to help determine the effects of snowmelt runoff.

$$K_{fact} = (1.292)\,[2.1\mathrm{x}10^{-6}\, f_p^{1.14}\,(12 - P_{om}) + 0.0325\,(S_{struc} - 2) + 0.025\,(f_{perm} - 3)] \tag{5.51}$$

in which

$$f_p = P_{silt}(100 - P_{clay}) \tag{5.52}$$

where	f_p	is the particle size parameter (unitless)
	P_{om}	is the percent organic matter (unitless)
	S_{struc}	is the soil structure index (unitless)
	f_{perm}	is the profile-permeability class factor (unitless)
	P_{clay}	is the percent clay (unitless).

In Equation 5.51 the factor (1.292) is needed to convert K_{fact} from the English units used in Golman et al. (1986) to the metric units used in this report. The soil structure index, S_{struc}, is equal to: 1 for very fine granular soil; 2 for fine granular soil; 3 for medium or coarse granular soil; 4 for blocky, platy, or massive soil. The profile-permeability class factor, f_{perm}, is equal to: 1 for very slow infiltration; 2 for slow infiltration; 3 for slow to moderate infiltration; 4 for moderate infiltration; 5 for moderate to rapid infiltration; 6 for rapid infiltration. Erickson (1977), as reported by Goldman et al. (1986), used the information from the nomograph and superimposed K-factors for 2% organic matter on a U.S. Department of Agriculture (USDA) soil textural classification triangle. Goldman et al. (1986) also presents tables to modify the results to account for

- soils with greater than 15% very fine sand
- soils with organic matter content different from that of 2%
- soils with rock (i.e., soil particle size greater than 2 mm) content greater than 14% by volume
- permeability
- structure.

Stewart et al. (1975), as reported by Mills et al. (1985), Mitchell and Bubenzer (1980), and Novotny and Chesters (1981), also developed a table indicating the general magnitude of the K-factor as a function of organic matter content and soil textural class. Their results are presented in Table 5.10.

Goldman et al. (1986) note that if site inspection or data analyses indicate significant variations in the soil erodibility, different K-factors can be assigned to different areas of the site. They also note that a simpler and more conservative approach is to use the highest value obtained for all parts of the site, because it may not be possible to know exactly what soils will be exposed or how varied the soils are.

Table 5.10. Soil Erodibility Factor K_{fact} (after Stewart et al. 1975)[(a)]

	P_{om}(%)		
Textural Class	<0.5	2	4
Sand	0.05	0.03	0.02
Fine sand	0.16	0.14	0.10
Very fine sand	0.42	0.36	0.28
Loamy sand	0.12	0.10	0.08
Loamy fine sand	0.24	0.20	0.16
Loamy very fine sand	0.44	0.38	0.30
Sandy loam	0.27	0.24	0.19
Fine sandy loam	0.35	0.30	0.24
Very fine sandy loam	0.47	0.41	0.33
Loam	0.38	0.34	0.29
Silt loam	0.48	0.42	0.33
Silt	0.60	0.52	0.42
Sandy clay loam	0.27	0.25	0.21
Clay loam	0.28	0.25	0.21
Silty clay loam	0.37	0.32	0.26
Sandy clay	0.14	0.13	0.12
Silty clay	0.25	0.23	0.19
Clay		0.13-0.2	

(a) The values shown are estimated averages of broad ranges of specific soil values. When a texture is near the border line of two texture classes, use the average of the two K_{fact} values. In addition, the values shown are commensurate with the English units used in the cited reference (and as used in the source-term module input files). To obtain analagous values in the metric units used in this report, the above values should be multiplied by 1.292.

5.3.3 Slope Length and Steepness Factor

The slope length and steepness factor (LS-factor) describes the combined effects of slope length (i.e., flow length) and slope gradient (i.e., grade or relief); it represents the ratio of soil loss per unit area on a site to the corresponding loss from a 22.1-m- (72.6-ft-) long experimental plot with a 9% slope. Slope length is defined as the distance from the point of origin of overland flow to the point where the slope decreases sufficiently for deposition to occur or to the point where runoff enters a defined channel (wet or dry). The slope steepness is the segment or site slope, usually expressed as a percentage. Although the LS-factor has traditionally been expressed as two parameters in the USLE, it is universally computed as a combined term (Mitchell and Bubenzer 1980; Goldman et al. 1986); which is why Equation 5.49 is written with the single factor S_{fact}.

Slope length and slope steepness strongly influence the transport of soil particles once the soil particles are dislodged by raindrop impact or runoff. Because the LS-factor can be defined to be substantially greater than unity, it can have a considerable effect on the predicted erosion. For this reason, averaging over large areas is not advised. In fact, Foster et al. (1980) suggest not basing the LS-factor solely on United States Geological Survey (USGS) topographic maps, as they usually suggest excessively long slope lengths.

Goldman et al. (1986) have mathematically expressed the LS-factor as follows:

$$S_{fact} = \left[65.41\left(\frac{S_{slope}^2}{a^2}\right) + 4.56\left(\frac{S_{slope}}{a}\right) + 0.065\right]\cdot(4.53\cdot10^{-4}L_{slope})^{m_{LS}} \tag{5.53}$$

in which

$$a = (S_{slope}^2 + 10{,}000)^{0.5} \tag{5.54}$$

where S_{slope} is the slope gradient (in percent) (unitless)

a is a factor in the LS-factor equation (unitless)

L_{slope} is the slope length (cm)

m_{LS} is the exponent in the LS-factor equation (unitless).

The exponent, m_{LS}, is equal to: 0.2 for $S_{slope} < 1\%$; 0.3 for $1\% \leq S_{slope} \leq 3\%$; 0.4 for $3.5\% \leq S_{slope} \leq 4.5\%$; 0.5 for $S_{slope} > 5\%$. Equations 5.53 and 5.54 have been expressed as a figure by a number of authors (e.g., Shultz et al. 1986; Novotny and Chesters 1981; Mitchell and Bubenzer 1980; Wischmeier and Smith 1978).

5.3.4 Vegetative Cover Factor

The vegetative cover factor (C-factor) is defined as the ratio of soil loss from land under specified vegetative or mulch conditions to the corresponding loss from tilled, bare soil (Goldman et al. 1986). Any vegetation or management condition that reduces the amount of soil exposed to raindrop impact will reduce erosion. In the USLE, the C-factor reduces the soil loss estimate according to the effectiveness of vegetation and mulch at preventing detachment and transport of soil particles. The effect of vegetation on erosion rates results from canopy protection, reduction of rainfall energy, and protection of soil by plant residues, roots, and mulches. When the surface is bare, the C-factor is considered to equal unity.

Typical values for C-factors are presented in Table 5.11. Many reports have been published defining the C-factor for numerous vegetative conditions. These documents include Goldman et al. (1986), Shultz et al. (1986); Mills et al. (1985), Kay (1983), Novotny and Chesters (1981), Mitchell and Bubenzer (1980), Wischmeier and Smith (1978, 1965), USDA (1975), Stewart et al. (1975), and Wischmeier (1976).

5.3.5 Erosion Control Practice Factor

The erosion control practice factor (P-factor) is defined as the ratio of soil loss with a given surface condition to soil loss with up-and-down-hill plowing. P-factor values involve treatments that retain liberated particles near the source and prevent further transport.[a] The P-factor accounts for the erosion control effectiveness of such land treatments as contouring, compacting, establishing sediment basins, and other control structures. At sites where there is or has been much human and vehicular traffic, the P-factor reflects the roughening of the soil surface by tractor treads or by rough grading, raking, or disking. Practices that reduce the velocity of runoff and the tendency of runoff to flow directly downslope reduce the P-factor (Goldman et al. 1986; Novotny and Chesters 1981).

(a) Note that protection of the soil surface against the impact of rain droplets and subsequent loss of soil particles is reflected in the C-factor (Novotny and Chesters 1981).

Table 5.11. C-Factor Values for the Universal Soil Loss Equation (after Kay 1983; USDA 1975; Wischmeier and Smith 1978; as reported by Goldman et al. 1986)

Type of Cover	C_{fact}	Soil Loss Reduction, %
None	1.0	0
Native vegetation (undisturbed)	0.01	99
Temporary seedings:		
90% cover, annual grasses, no mulch	0.1	90
Wood fiber mulch, 3/4 ton/acre (1.7 t/ha), with seed[(a)]	0.5	50
Excelsior mat, jute[(a)]	0.3	70
Straw mulch [(a)]		
1.5 tons/acre (3.4 t/ha), tacked down	0.2	80
4 tons/acre (9.0 t/ha), tacked down	0.05	95
(a) For slopes up to 2:1.		

Table 5.12 presents typical values for sites with varying practice conditions and structures. Note that most of the P-factor values are close to unity; changing the surface conditions does not provide much direct reduction in P-factor, although other USLE factors may change and may have a significant effect on the amount of soil loss.

5.3.6 Converting USLE to Water Erosion Rate

The average annual soil loss, A_{loss}, calculated by the USLE is in units related to a soil mass basis (i.e., t ha^{-1} yr^{-1}). The source-term release module requires the volumetric water erosion rate, E, which has units related to a soil volume basis (i.e., cm^3 cm^{-2} yr^{-1}). Therefore, E, is calculated by the conversion expression

$$E = \frac{(1x10^{-2})\, A_{loss}}{\beta_s} \tag{5.55}$$

where E is the volumetric water erosion rate (cm yr^{-1}).

(In Equation 5.55, the factor $1x10^{-2}$ converts t ha^{-1} yr^{-1} to g cm^{-2} yr^{-1}.)

Table 5.12. P-Factor Values for Various Practice Conditions (after Ports 1973, as reported by Novotny and Chester 1981)

Erosion Control Practice	P_{fact}
Surface Condition with No Cover	
Compact, smooth, scraped with bulldozer or scraped up and down hill	1.30
Same as above, except raked with bulldozer and root-raked up and down hill	1.20
Compact, smooth scraped with bulldozer or scraped across the slope	1.20
Same as above, except raked with bulldozer and root-raked across slope	0.90
Loose, as a disked plow layer	1.00
Rough irregular surface, equipment tracks in all directions	0.90
Loose with rough surface >0.3 m depth	0.80
Loose with smooth surface >0.3 m depth	0.90
Structures	
Small sediment basins:	
0.09 basins/ha	0.50
0.13 basins/ha	0.30
Downstream sediment basins:	
With chemical flocculants	0.10
Without chemical flocculants	0.20
Erosion control structures:	
Normal rate usage	0.50
High rate usage	0.40
Strip building	0.75

5.4 Mass Loss Expressions for Individual Loss Routes

The processes that can cause contaminant mass (or activity) to be lost from the source zone are assumed to be first-order radioactive decay/degradation within the source zone, vertical leaching into the vadose zone below the source zone along with the percolating vadose zone water, wind suspension of contaminated soil particles from the soil surface, water erosion of contaminated soil particles from the soil surface, and volatilization from the soil surface (potentially through an uncontaminated layer of soil above the source zone). Hence the overall instantaneous rate of change of contaminant mass in the source zone for contaminant *i* is given by

$$\frac{dM_i}{dt} = \left[\frac{dM_i}{dt}\right]_{decay} + \left[\frac{dM_i}{dt}\right]_{leach} + \left[\frac{dM_i}{dt}\right]_{susp} + \left[\frac{dM_i}{dt}\right]_{eros} + \left[\frac{dM_i}{dt}\right]_{vol} \tag{5.56}$$

This section discusses the theory developed to describe the individual terms on the right-hand side of Equation 5.56 when each loss process acts alone.

5.4.1 First-Order Decay

The degradation or radioactive decay process is assumed to follow first-order kinetics, which means that the rate of loss of mass at any given time is directly proportional to the mass present at that time. The mass flux equation for loss from the source zone by decay/degradation alone is then given by

$$\left[\frac{dM_i}{dt}\right]_{decay} = -\lambda_i M_i \tag{5.57}$$

Each contaminant is assumed to have a unique overall first-order decay coefficient λ_i. Note that Equation 5.57 is based on the assumption that the first-order decay coefficient is independent of in which phase (aqueous, solid-sorbent, vapor, NAPL) the contaminant resides.

5.4.2 Leaching

The leaching process is assumed to occur by advective transport of the aqueous contaminant out of the bottom face of the source zone along with the percolating vadose zone water. This means that the rate of loss of mass at any given time is given by the volumetric flux of water out of the source zone face multiplied by the aqueous concentration of the contaminant in the water at that time:[a]

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\,Q_w\,C_{wi} \tag{5.58}$$

The volumetric water flux, in turn, can be expressed in terms of the Darcy water flux density (i.e., Darcy velocity) of the percolating water and the area of the bottom face of the source zone:

(a) Note that, in a strict sense, the variable Q_w should really be referred to as the aqueous solution flux (which contains water and dissolved constituents). However, because aqueous solutions are typically volumetrically dilute with respect to their dissolved constituents, it is quite common to refer to the aqueous solution flux as the water flux.

$$Q_W = q_w\, A \tag{5.59}$$

By substituting Equation 5.59 into Equation 5.58, the mass flux equation for loss from the source zone by leaching alone can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\, q_w\, A\, C_{wi} \tag{5.60}$$

When a NAPL phase exists in the source zone, the aqueous concentration of the contaminant is controlled by the composition of the NAPL phase. In this case, the source-term release module calculates the value of C_{wi} in Equation 5.60 by the phase partitioning theory described in Section 2.2.4 (which uses different methods, depending on the mole fraction [or concentration] of the contaminant in the NAPL phase).

When no NAPL phase exists in the source zone, the aqueous concentration can be calculated by a simple phase partitioning relation (i.e., Equation 2.7 in Section 2.2.3). When leaching is the only loss process occurring, the vertical thickness, (z_b-z_t), of the source zone is constant in time. In this case, the volume of the source zone is given by

$$V = A \cdot (z_b - z_t) \tag{5.61}$$

where z_b is the distance from the initial position of the soil surface to the bottom of the source zone at any time (cm)

z_t is the distance from the initial position of the soil surface to the initial position of the top of the source zone (i.e., initial thickness of clean layer) (cm).

Substituting Equation 5.61 into Equation 2.7, the aqueous concentration can be given by

$$C_{wi} = \frac{M_i}{\theta_w\, R_i\, A\, (z_b - z_t)} \tag{5.62}$$

Now, substituting Equation 5.62 into Equation 5.60, the mass flux equation for loss from the source zone by leaching (when no NAPL is present) can be expressed as

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\, \frac{q_w\, M_i}{\theta_w\, R_i\, (z_b - z_t)} \tag{5.63}$$

Recall that the retardation factor, R_i, in Equation 5.63 was defined in general terms by Equation 2.5. It is worthwhile to note that for the contaminated vadose zone source zone, the solid-sorbent bulk density in Equation 2.5 is equal to the soil bulk density, β_s.

The above equations were for leaching from contaminant source zones that have not been subjected to remediation methodologies. However, they are also appropriate to scenarios where a remediation methodology has been implemented that only alters the source zone by changing the value of some parameter in the aforementioned model (e.g., reducing the contaminant inventory, reducing the water flux through the zone, increasing the sorption coefficient).

Two additional remediation methodologies implemented in the source-term release module require special theory (i.e., formulations that differ from the mass flux expressions for unremediated scenarios), because leaching occurs by fundamentally different mechanisms than those described by the previous equations. The first additional remediation methodology is ISV, which is a methodology that consists of converting the contaminant source zone into a glass waste form. The resulting glass waste form is a cracked (rather than a solid) monolith, with much internal surface area exposed to percolating vadose-zone water. Contaminants are released as the glass slowly dissolves into the percolating water from all of its exposed surface area. The second additional remediation methodology is ISS, which is a methodology that consists of injecting liquid grout material into the pores of the source zone and allowing it to solidify into a solid microporous monolith. Contaminants are released as they slowly diffuse through the grout to the outer surface boundary of the monolith, where they first encounter water percolating down through the vadose zone.

For times after an ISV remediation methodology has been implemented, the contaminant release mechanism is dissolution of the cracked glass waste form. The glass waste form is assumed to be a so-called "well-mixed reactor." Therefore, the mass flux equation for loss from the source zone by leaching alone for an ISV waste form is given by

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\frac{r_g A_{sg} M_i}{\rho_g V_g} \tag{5.64}$$

where r_g is the mass dissolution rate of glass in an ISV waste form per surface area (g yr^{-1} cm^{-2})
A_{sg} is the total surface area of cracked glass in an ISV waste form (cm^2)
ρ_g is the density of glass in an ISV waste form (g cm^{-3})
V_g is the volume of cracked glass in an ISV waste form (cm^3).

Note that A_{sg} and V_g would not be constant in real-world situations, but instead would be changing over time as the glass dissolves. This means that to be accurate, Equation 5.64 would need to be further developed by substituting into it appropriate expressions for how the surface area and volume change as a function of time. In general, these expressions would depend on the initial shape and size of the waste form, and how it is assumed to crack over time. For all but simple initial shapes and cracking patterns, it would be extremely difficult, if not impossible, to derive analytical expressions for $A_{sg}(t)$ and $V_g(t)$.

Therefore, the equation implemented in the module assumes the following idealization. When leaching is the only loss process occurring, the overall total concentration of a contaminant in the glass is always given by its initial value:

$$C_{Ti} = \frac{M_{io'}}{V_{go}} \tag{5.65}$$

where $M_{io'}$ is the total mass or activity of contaminant *i* in the source zone at the time the zone was subjected to ISV remediation (g or Ci)

V_{go} is the initial volume of cracked glass in an ISV waste form (cm^3).

If it is assumed that the surface area of the glass is always equal to its initial value, the mass flux equation for loss from the source zone by leaching alone for an ISV waste form is given by

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\frac{r_g A_{sgo} M_{io'}}{\rho_g V_{go}} \tag{5.66}$$

where A_{sgo} is the initial total surface area of cracked glass in an ISV waste form (cm^2).

This idealization implicitly assumes that the decrease in surface area caused by the dissolving glass pieces shrinking is just equal to the increase in surface area caused by additional glass cracking.

Note further that when a site is remediated with an ISV process, all the organic contaminants are vaporized during the vitrification process and no longer exist in the resulting ISV waste form. Therefore, simulations with organic contaminants and an ISV waste form present from time zero should not be conducted. If the simulated scenario contains a baseline period before an ISV process is implemented, the masses of all organic contaminants should be zero for all times after implementation of the ISV.

For times after an ISS remediation methodology has been implemented, the contaminant release mechanism is diffusion through the grout within the source zone to the outer boundary of the solidified waste form. Therefore, the mass flux equation for loss from the source zone by leaching alone for an ISS waste form is given by

$$\left[\frac{dM_i}{dt}\right]_{leach} = -M_{io''}\left(\frac{A_s}{V}\right)\sqrt{\frac{D_{gi}}{\pi t}} \tag{5.67}$$

where $M_{io''}$ is the total mass or activity of contaminant *i* in the source zone at the time the zone was subjected to ISS remediation (g or Ci)

D_{gi} is the effective diffusion coefficient of contaminant *i* within an ISS waste form ($cm^2\ yr^{-1}$).

This equation is the solution to the diffusion equation for mass lost through an infinite plane that bounds a semi-infinite solid source, when no degradation/decay occurs (Godbee et al. 1980). The mass flux calculated by Equation 5.67 is approximately equal to that coming from a finite solid source for early times. However, at later times, Equation 5.67 will overpredict the mass flux by an increasing amount as time goes on. Note also that Equation 5.67 depends on the mass in the source zone at the time when the ISS methodology was implemented in the zone (i.e., when grout was injected into the zone), rather than on the mass in the source zone at any given time (as in the previous mass flux equations). This arises from the fact that the conceptual model used here requires that a spatial gradient in concentration be present within the waste form. This is in direct opposition to the "well-mixed reactor" assumption used to derive mass flux expressions in all of the other scenarios dealt with. This contradiction will cause some restrictions regarding additional loss routes that can be accommodated when formulating expressions for mass flux for multiple, concurrent loss pathway scenarios. Furthermore, because Equation 5.67 depends on M_{io^*} rather than M_i, partial failure of an ISS waste form cannot be simulated (i.e., simulating partial failure cannot be done by merely adjusting some parameter in Equation 5.67). However, total failure of an ISS waste form at some designated time can be simulated. In this case the leaching term reverts back to Equation 5.60 or 5.63 at the time of failure; and the source zone begins to be treated as a "well-mixed reactor" again (with mass equal to the mass remaining in the ISS waste form when it failed). In addition, this dependence on M_{io^*} (rather than M_i) also means that mass cannot be added to the source zone during a simulation through chain decay from parent contaminants. Additional special theory is used to accommodate daughter product accumulation and loss; but this is discussed in the section on multiple concurrent loss processes.

In certain environments (e.g., where the vadose zone water flux density is very low), Equations 5.66 and 5.67 may predict greater leaching loss fluxes than the equations for unremediated source zones (i.e., Equations 5.60 or 5.63). This is not realistic; and happens only because Equations 5.66 and 5.67 assume that the rate-limiting process is the release from the waste form. What is actually happening in the real environment is that movement in the soil water would be the rate-limiting step. Hence, the module compares mass fluxes predicted by the equations for remediated and unremediated scenarios and uses the smaller loss flux.

5.4.3 Wind Suspension or Water Erosion

Contaminant mass can also be lost from the source zone by removal of soil (which contains contamination) from the upper surface of the zone by natural processes. Particles of contaminated soil can be suspended in the air and moved away from the source zone by wind action, or they can be dislodged from the soil surface by water erosion and moved away from the source zone suspended in overland runoff. While both of these processes are governed by unique mechanisms, the ultimate mass loss flux equations for both processes have similar mathematical forms. Therefore, both of these contaminant loss pathways will be discussed in this one section, even though the resulting equations presented in this section are strictly for mass loss when only one of these processes is occurring.

First, consider scenarios where the soil is contaminated all the way up to the soil surface. These surface removal processes then strip off bulk soil from the top of the contaminant source zone (which is exposed to the wind or the overland runoff water). Consequently, these scenarios can be characterized by surface soil removal rates due to wind suspension, S, and water erosion, E. These rates are defined as the depth of surface soil lost per time (which is equivalent to the volume of surface soil lost per time per area of surface). Because these processes strip off a depth of the soil itself, they remove all contaminant that is contained in the bulk soil. Therefore, the mass loss flux is not affected by how the contaminant is partitioned between aqueous, solid-sorbent, vapor, or NAPL phases. The contaminant mass flux to a surface soil removal pathway is then given by

$$\left[\frac{dM_i}{dt}\right]_{\text{surf rem}} = -\ (\text{Surface Soil Removal Rate})\ A\ C_{Ti} \tag{5.68}$$

The volume of the source zone is given by

$$V = A\ h \tag{5.69}$$

where h is the thickness of the contaminant source zone (cm).

Substituting Equation 5.69 into Equation 2.2, and then substituting the resulting equation into Equation 5.68, we obtain

$$\left[\frac{dM_i}{dt}\right]_{\text{surf rem}} = -\ \frac{(\text{Surface Soil Removal Rate})\ M_i}{h} \tag{5.70}$$

Note that the thickness, h, of the source zone is not a constant in these cases, but instead decreases linearly with time because the surface soil removal process is constantly stripping away soil from the top of the zone. When this time dependence is explicitly written, the mass flux equations for loss from the source zone by either wind suspension alone or water erosion alone are given by

$$\left[\frac{dM_i}{dt}\right]_{\text{susp}} = -\ \frac{S\,M_i}{z_b - St} \tag{5.71}$$

and

$$\left[\frac{dM_i}{dt}\right]_{\text{eros}} = -\ \frac{E\,M_i}{z_b - Et} \tag{5.72}$$

On the other hand, there can also be scenarios where the soil is not contaminated all the way up to the soil surface. If a clean uncontaminated soil layer exists above the contaminant source zone, these surface soil removal processes will be stripping away clean soil. Therefore, the contaminant mass flux is zero for wind suspension and water erosion as long as a clean layer remains. However, as the clean layer is gradually removed, the contaminant source zone may eventually become exposed. When the clean layer is completely eroded away, mass fluxes to these two pathways will become non-zero according to Equations 5.71 and 5.72.

Note, that deposition of clean soil particles onto the top of the site (by either wind or water) can also be simulated by the module by entering negative values of S or E. In these cases, the module sets the contaminant mass flux for wind suspension and water erosion to zero.

5.4.4 Volatilization

The conceptual model for volatilization from the vadose zone source zone is as follows. Only contaminants with modified (dimensionless) Henry's Law constants $\geq 10^{-7}$ are assumed to volatilize.(a) There is no contaminant gas generation (e.g., caused by microbial metabolic processes) in the source zone, as there sometimes is in landfills. There may initially be a layer of uncontaminated soil above the contaminant source zone. If this clean layer exists initially, it is assumed to be relatively porous (the same as the rest of the soil in the source zone); i.e., it is not a compacted cap layer that has gaseous permeability or vapor diffusion properties that are significantly lower than those within the contaminated zone. The source zone is assumed to be a so-called "well-mixed reactor," which means that the vapor concentration of any contaminant in the air-filled pores is spatially uniform throughout the source zone. Hence, no vapor diffusion takes place within the source zone. Contaminant vapor is assumed to diffuse through the clean layer from the uppermost edge of the source zone toward the soil surface (and then be lost as volatilization into the atmosphere). In addition, note that even though the contaminant also resides in the aqueous phase in the source zone, it is assumed that upward diffusive transport in the water phase is negligible compared to the vapor transport. Furthermore, it is assumed that contaminant vapor diffuses through the clean layer quickly enough that contaminant within the source zone cannot redistribute itself fast enough to maintain the source zone at its current dimensions (with the overall total concentration falling over time uniformly at all locations due to the volatilization process). Rather, the conceptual model assumes that contaminants are preferentially stripped away from the uppermost end of the source zone to satisfy the volatilization flux. This means that the thickness of the source zone decreases over time as the uppermost boundary recedes to deeper depths (and the clean layer gets thicker). The vapor diffusion process is assumed to be quasi-steady-state, which means that the flux is always described by a steady-state diffusion expression, even though the thickness of the diffusion zone is changing over time and the contaminant's vapor concentration in the source zone may change over time, as the top of the source zone recedes. This conceptual model (which predicts recession of an infinitely steep contamination front) is an idealization of the actual diffusive stripping process (which would predict recession of a sigmoidally shaped front).

If a clean layer of soil does not initially exist above the contaminated source zone, the stripping away of contaminants from the top of the source zone (as described above) quickly creates one. When

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(a) This screening is accomplished by assigning a value of zero to the effective vapor diffusion coefficients of all contaminants with $K_{Hi} < 10^{-7}$

volatilization is the only loss process occurring, the thickness of this clean layer continues to grow over time, once it has been formed.

The theory implemented in the source-term release module to estimate the mass flux to volatilization is based on the derivations of Thibodeaux and Hwang (1982). Their conceptual model for the source zone is similar to that described above, except that in their model a clean layer always exists initially, the source zone always contains a NAPL phase, and the contaminant mass partitioned into the aqueous and solid-sorbent phases is negligible. Their previous work had only considered a pure NAPL phase (i.e., a NAPL phase composed of only one constituent). Thibodeaux and Hwang (1982) extend their previous theory to apply to contaminants that are present as dilute constituents of a NAPL phase mixture.

With the conceptual model of Thibodeaux and Hwang (1982), the mass flux equation for volatilization from a source zone through a clean layer is given by

$$\left[\frac{dM_i}{dt}\right]_{vol} = -\frac{A\,D_{vi}\,C_{vi}}{z} \tag{5.73}$$

where D_{vi} is the effective vapor diffusion coefficient of contaminant i in soil (cm^2 yr^{-1})

z is the distance from the initial position of the soil surface to the top of the source zone at time t (cm).

With volatilization from the upper boundary of the source zone being the only loss route, the overall total concentration of a contaminant in the source zone is always equal to its initial concentration. Using this fact, the rate of reduction of contaminant mass in the source zone due to recession of the top boundary is given by

$$\left[\frac{dM_i}{dt}\right]_{recession} = C_{Ti}\,\frac{dV}{dt} = -C_{Ti}\,A\,\frac{dz}{dt} = -\frac{M_{io}}{A\,(z_b - z_t)}\,A\,\frac{dz}{dt} = -\frac{M_{io}}{(z_b - z_t)}\,\frac{dz}{dt} \tag{5.74}$$

Based on mass balance considerations for any contaminant individually, the volatilization mass loss rate must equal the rate of reduction of contaminant mass in the source zone due to recession of the top boundary. Equating the right-hand sides of Equations 5.73 and 5.74, and rearranging the resulting equation, gives the recession rate of the top of the source to be

$$\frac{dz}{dt} = \frac{A\,D_{vi}\,C_{vi}\,(z_b - z_t)}{M_{io}\,z} \tag{5.75}$$

Assuming that the contaminant's vapor concentration in the source zone also remains constant in time, Equation 5.75 can be rearranged and integrated to obtain an analytical expression for the clean layer thickness, z, as a function of time. When this expression is substituted into Equation 5.73, the mass flux equation for volatilization becomes

$$\left[\frac{dM_i}{dt}\right] = -\frac{A\ D_{vi}\ C_{vi}}{\sqrt{z_t^2 + \dfrac{2\ A\ D_{vi}\ C_{vi}\ (z_b - Z_t)\ t}{M_{io}}}} \tag{5.76}$$

There are, however, a number of reasons why the theory of Thibodeaux and Hwang (1982) is not adequate for our purposes. Firstly, their theory does not explicitly describe how to predict loss flux from source zones that do not contain a NAPL phase (or that contain one initially that disappears during the course of the simulation). Secondly, their theory is not applicable to a contaminant when it is an intermediate or primary constituent of the NAPL phase. In the limit of dilute NAPL-phase concentration for the contaminants under study, Thibodeaux and Hwang (1982) appropriately used a type of Henry's Law to represent the contaminant vapor concentration in Equations 5.73 through 5.76. But they did not specify how to do the calculations when Henry's Law was not valid. Thirdly, because this theory is merely a simple modification of their theory for a pure NAPL phase, it predicts the rate of increase of clean layer thickness based on the removal of only the contaminant being analyzed at that time. Hence, if multiple contaminants in a NAPL phase are to be analyzed, their theory would only be internally self-consistent if all other constituents of the NAPL phase are volatilizing at a rate that would cause the clean layer thickness to increase at the same rate. This clearly would not be true in general. Fourthly, because their equations for a given contaminant assume that the contaminant concentration in the NAPL phase is constant in time, their theory would only be internally self-consistent if other constituents of the NAPL phase are being removed at rates that keep the relative composition of the remaining NAPL constant in time. This clearly also would not be true in general.

Therefore, when volatilization is the only mass loss process, a more appropriate way for the source-term release module to calculate the mass flux is as follows. In general, the mass flux equation for volatilization from a source zone through a clean layer is still given by Equation 5.73. However, when mass balance arguments are made as in Thibodeaux and Hwang (1982) (i.e., for each contaminant individually), a separate source zone boundary recession rate is calculated for each contaminant. If the module actually used all of these individual recession rates, what this would mean in terms of predicted behavior in the overall problem scenario is that a vertical spatial gradient in NAPL-phase composition would immediately develop as more highly volatile compounds are preferentially removed from the upper portions of the source zone. While this may be physically reasonable, it is inconsistent with our assumption that the source zone is a "well-mixed reactor." Because the NAPL phase partitioning theory assumes that all NAPL components are in a zone of the same size, as soon as a spatial gradient in NAPL-phase composition developed (because of the recession rate theory), the module would be calculating NAPL-phase mole fractions that are inconsistent with this conceptualization (and errors caused by the inconsistency would be compounded over time).

If a contaminant is not a component of the NAPL phase, its phase partitioning behavior does not depend on any components of the NAPL phase, or any other contaminants in general. Furthermore, all contaminants that cannot be part of a NAPL phase (i.e., contaminants with $K_{Hi} < 10^{-7}$) are assumed to be nonvolatile (i.e., are assigned values of D_{vi} that are identically equal to zero); which means that there is no change in position of the top boundary of the source zone due to volatilization when calculated individually for these contaminants. Many of these contaminants can decay/degrade into other contaminants, but none of these other contaminants are contaminants that may be a component of the NAPL phase. In addition, no contaminant that may be a component of the NAPL phase can decay/degrade into any of the non-NAPL phase contaminants. All of this means that the overall source zone can be conceptualized as two separate problems: one that consists of all of the non-NAPL contaminants and one that consists of all the NAPL components. The problem that consists of all non-NAPL contaminants will have a single, "well-mixed reactor" source zone over time by default. For the problem that consists of all NAPL-phase components, the source-term release module uses the individual recession rates calculated for each component of the NAPL phase to obtain a single overall rate of recession of the upper source zone boundary for these contaminants.

To do this, first consider that the volume of the source zone at any time is given by Equation 5.69, and the thickness of the source zone at any time is given by

$$h = z_b - z \tag{5.77}$$

Using Equations 5.69 and 5.77, the rate of reduction of contaminant mass in the source zone due to recession of the top boundary is given by

$$\left[\frac{dM_i}{dt}\right]_{\text{recession}} = C_{Ti}\frac{dV}{dt} = -C_{Ti}A\frac{dz}{dt} = -\frac{M_i}{A(z_b - z)}A\frac{dz}{dt} = -\frac{M_i}{(z_b - z)}\frac{dz}{dt} \tag{5.78}$$

(Note that Equation 5.78 is analogous to Equation 5.74.) Again, equating the right-hand sides of Equations 5.73 and 5.78, and rearranging the resulting equation, gives the recession rate of the top of the source to be

$$\frac{dz}{dt} = \frac{A\,D_{vi}\,C_{vi}\,(z_b - z)}{M_i\,z} \tag{5.79}$$

Because the vapor concentration in Equation 5.79 is not a simple function of the contaminant mass when a NAPL phase is present, and because the contaminant mass is not constant in time, Equation 5.79 cannot be rearranged and integrated to obtain a general analytical expression for the clean layer thickness, z, as a function of time. Hence, even when volatilization is the only loss process occurring, the source-term release module must solve a mathematical problem (for each contaminant) that consists of simultaneously solving Equations 5.73, and 5.79.

For contaminants that are components of the NAPL phase, the module then calculates a single updated position of the top boundary of the source zone by taking an average of the individual updated positions predicted by the solution of Equation 5.79, weighted by the mole fraction of the contaminant:

$$z = \sum_{i=1}^{n_{cn}} X_{oi} \, z_i \tag{5.80}$$

(In Equation 5.80, the subscript *i* on the variable z denotes that this is the updated position of z as calculated for an individual contaminant.) With this approach, contaminants that are present in the NAPL phase in higher proportions will have a greater influence on how much the top boundary of the source zone recedes.

When a NAPL phase exists in the source zone, the vapor concentration of the contaminant is controlled by the composition of the NAPL phase. In this case, the source-term release module calculates the value of C_{vi} in Equations 5.73 and 5.79 by the phase partitioning theory described in Section 2.2.4 (which uses different methods, depending on the mole fraction [or concentration] of the contaminant in the NAPL phase).

When no NAPL phase exists in the source zone, the vapor concentration can be calculated by a simple partitioning relation (i.e., Equation 2.8 in Section 2.2.3). If the volume of the source zone is given by Equation 5.69, and the thickness, h, of the source zone is given by Equation 5.77, these equations can be substituted into Equation 2.8, and the resulting expression can be substituted into Equation 5.73. Therefore, in this case (when volatilization is the only loss process occurring and no NAPL phase exists), the mass flux equation for contaminant loss from the source zone by volatilization is given by

$$\left[\frac{dM_i}{dt}\right]_{vol} = -\frac{D_{vi} K_{Hi} M_i}{\theta_w R_i (z_b - z) z} \tag{5.81}$$

Similarly, the equation giving the rate of recession of the top boundary of the source zone (when no NAPL phase exists) is given by

$$\frac{dz}{dt} = -\frac{D_{vi} K_{Hi}}{\theta_w R_i z} \tag{5.82}$$

The above derivations relate to the case where a clean layer always exists above the contaminated source. When the soil is initially contaminated all the way up to the soil surface (i.e, when $z_t = 0$) Equation 5.73 or 5.81 would predict an infinite volatilization mass flux initially because the thickness of the diffusion zone, z, would be zero. This is, of course, not what would happen in the real-world situation. In reality, a concentration gradient immediately develops at the soil surface, and volatilization loss is governed by a transient-state diffusion process. Contaminant mass is stripped away from the surface and a "relatively clean" layer begins to develop at the surface (i.e., there is a region near the surface, above the sigmoidally-shaped contaminant front, where the contaminant concentration is very close to zero). Eventually, when this region becomes thick enough, the volatilization behavior becomes more like that predicted by the idealized conceptual model used in the module. So, when no clean layer exists initially, the module uses an alternate expression for the volatilization flux (instead of Equation 5.73 or 5.81) to calculate a bounding value for this flux at the initial time step. Furthermore, even when a clean layer exists (either initially, or when one forms at subsequent time steps), the module uses this same alternate expression to calculate a bounding value for the flux at time steps when Equation 5.73 or 5.81 would predict finite, but unreasonably high, values of flux (because z is nonzero but still very small). This alternate expression is derived from the transient-state diffusion model described above. This model, called the "Contaminated Soil Gradient Model," was one of the volatilization scenarios that users could select for the vadose zone source zone in previous versions of MEPAS (see Droppo and Buck 1996). The mass flux equation for contaminant loss by volatilization for this model is given by

$$\left[\frac{dM_i}{dt}\right]_{vol} = -A\,C_{Tio}\sqrt{\frac{K_{Hi}\,D_{vi}}{\theta_w\,R_i\,\pi\,t}} \qquad (5.83)$$

where C_{tio} is the value of overall total concentration of contaminant *i* used at the beginning of a time step in the bounding calculation for volatization (g cm^{-3} or Ci cm^{-3}).

Equation 5.83 gives the instantaneous volatilization loss at time t since the initial incorporation of contaminant into the soil at a spatially uniform overall total concentration of C_{Tio}. Note that because of the infinite concentration gradient at the soil surface at $t = 0$, Equation 5.83 also predicts an infinite flux at $t = 0$. However, this infinite flux would only last for an infinitesimally small time. Therefore, the "Contaminated Soil Gradient Model" actually calculates an average value of the flux for a given time period, which we will take to be the length of our time step. The mass flux equation for average contaminant loss (over a time period Δt) by volatilization for this model is given by

$$\left[\frac{dM_i}{dt}\right]_{vol}^{ave} = -2\,A\,C_{Tio}\sqrt{\frac{K_{Hi}\,D_{vi}}{\theta_w\,R_i\,\pi\,\Delta t}} \qquad (5.84)$$

The value calculated by Equation 5.84 is considered an upper bounding value because we realize that the volatilization rate should not be greater than what would be predicted by the transient-state diffusion problem at initial times, and because of the way we calculate C_{Tio}, and the fact that we use Δt. Equations 5.83 and 5.84 were developed under the assumption that no NAPL phase exists in the source zone. Implicit in these equations is the idea that the contaminant's vapor concentration can be calculated by simple partitioning theory (i.e., Equation 2.8). When Equation 5.84 is used to calculate the values for mass loss at a particular time step, C_{Tio} is calculated by

$$C_{Tio} = \frac{M_i}{A\ (z_b - z)} \tag{5.85}$$

This means that when a NAPL phase is present, the implicit vapor concentration in Equation 5.84 is greater than what it would really be because all of the contaminant mass is considered as part of the aqueous, sorbed, and vapor phases only. So the flux value calculated by Equation 5.84 is biased to be an upper bound. Furthermore, by using Equation 5.84 for any time step, the module is in effect calculating a value that is commensurate with the idea that the contaminant's mass at the beginning of that time step has been redistributed all the way up to the soil surface again. Again, this produces a value biased to be an upper bound compared to using the actual value of t.

Substituting Equation 5.85 into Equation 5.84, the volatilization loss of a contaminant, as calculated by the bounding value, is given by

$$\left[\frac{dM_i}{dt}\right]_{vol}^{ave} = -\frac{2\,M_i}{(z_b - z)} \sqrt{\frac{K_{Hi}\,D_{vi}}{\theta_w\,R_i\,\pi\,\Delta t}} \tag{5.86}$$

Equating the right-hand sides of Equations 5.78 and 5.86 according to mass balance arguments, the rate of recession of the top boundary of the source zone based on an individual contaminant (when a bounding value for volatilization is used) is given by

$$\frac{dz}{dt} = 2\sqrt{\frac{K_{Hi}\,D_{vi}}{\theta_w\,R_i\,\pi\,\Delta t}} \tag{5.87}$$

Equation 5.87 is solved to get an updated value of z for any contaminant where a bounding value is used for volatilization loss. These values of z_i for NAPL-phase components are then used by the module in conjunction with updated values of z for other NAPL-phase components (obtained by solving either Equation 5.79 or 5.82) to calculate the single rate of recession of the top boundary of the source zone for NAPL components by using Equation 5.80.

To summarize, for each contaminant, the mass flux equation for contaminant loss from the source zone by volatilization is given by Equation 5.73 when a NAPL phase exists in the source zone, and Equation 5.81 when no NAPL phase exists in the source zone, unless this value is greater than the bounding value calculated by Equation 5.86. In this event, the mass flux equation is given by Equation 5.86. In addition, when bounding values are not used for volatilization fluxes, the rate of change in position of the upper boundary of the source zone (which will recede due to volatilization losses), based on an individual contaminant, is given by Equation 5.79 when a NAPL phase exists in the source zone, and Equation 5.82 when no NAPL phase exists in the source zone. If a bounding value is used for the volatilization flux, the rate of change in position of the upper boundary of the source zone, based on an individual contaminant, is given by Equation 5.87. For contaminants that are components of a NAPL phase, Equation 5.80 is then used to calculate a single updated position of the top boundary of the source zone for all of the NAPL-phase components.

5.5 Mass Loss Expressions for Multiple Concurrent Loss Routes

In general, first-order decay/degradation, leaching, wind suspension, water erosion, and volatilization could all be happening concurrently; and some type of remediation methodology could be implemented at some point during the simulation time. The multiple, concurrent processes can interact; which can cause the mathematical expression for a given term in Equation 5.56 to be different from what it would be if that process was the only one removing mass from the source zone. When processes occur simultaneously, the appropriate mathematical formulations are as follows.

The mass flux term for loss from the source zone by decay/degradation is still given by the expression in Equation 5.57. This is true even for the scenario in which an ISS remediation methodology has been implemented. Recall that the conceptual model for this scenario assumes that a spatial gradient in concentration develops inside the waste form as contaminants diffuse out of it. However, it is true that

$$\left[\frac{dM_i}{dt}\right]_{decay} = \left[\frac{d}{dt}\right]_{decay} \int_V C_{Ti}\,dV = \int_V \left[\frac{dC_{Ti}}{dt}\right]_{decay} dV = -\lambda_i \int_V C_{Ti}\,dV = -\lambda_i M_i \tag{5.88}$$

which demonstrates that Equation 5.57 is still valid. However, for an ISS scenario, if decay products are also contaminants of interest, the mass of decay products produced by the decay term (Equation 5.57) for the parent contaminant is not added back into the mass of the source zone for consideration in subsequent time steps. The necessity of this restriction arises from the fact that the mass flux term for leaching from an ISS waste form is based on spatial concentration gradients and contaminant masses in the source zone at the initial time, rather than at the actual time. (This is different than the way the source-term release module handles the accumulation and subsequent loss of decay products of concern for other scenarios.)

The term for leaching can take on one of several different forms depending on the particular scenario being simulated (e.g., whether a NAPL phase exists, whether a clean soil layer exists above the source zone, whether a remediation methodology has been implemented). In general form, the mass flux term for loss from the source zone by leaching is still given by Equation 5.60. When a NAPL phase exists in the source zone, the mass flux term for loss from the source zone by leaching is still calculated by Equation 5.60 directly, with the value of C_{wi} calculated form the phase partitioning theory described in Section 2.2.4, as before.

When no NAPL phase exists in the source zone, the mass flux term for leaching may take on a number of forms. When no ISV or ISS remediation methodology has been implemented, consider that the aqueous concentration of the contaminant is given by Equation 2.7, and the volume of the source zone is given by Equation 5.69. Substituting Equations 2.7 and 5.69 into Equation 5.60, we obtain

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\frac{q_w M_i}{\theta_w R_i h} \tag{5.89}$$

Now all that remains is to determine the correct way to express the thickness, h, of the source zone that appears in Equation 5.89. The position of the lower boundary of the source zone is constant in time. On the other hand, the position of the upper boundary of the source zone may be changing due to volatilization and/or wind suspension and water erosion. Firstly, consider a scenario where a clean layer of soil exists above the source zone initially. Depending on the relative rates of wind suspension, water erosion, and volatilization, it could be the case that the clean layer will always exist during the simulated time frame (and maybe even grow in thickness); or it could be the case that the clean layer will eventually be stripped away at some time during the simulated time frame. Secondly, consider a scenario where a clean layer of soil does not exist above the source zone initially. Again, depending on the relative rates of wind suspension, water erosion, and volatilization, a clean layer may never develop; or it may develop and always exist thereafter during the simulated time frame; or it may develop but eventually be stripped away at some time during the simulated time frame. As long as a clean layer is present, the process controlling the thickness of the source zone is volatilization. When no clean layer is present, the processes controlling the thickness of the source zone are wind suspension and/or water erosion. The criterion that must be used to determine which of these two regimes the system is in is a comparison between the position of the top of the source zone, z, and the position of the soil surface, which can be expressed as (S+E)t. Hence, the thickness of the source zone is given by

$$h = \begin{cases} z_b - z & \text{for } z > (S+E)t \\ z_b - (S+E)t & \text{for } z \leq (S+E)t \end{cases} \tag{5.90}$$

Substituting the appropriate expression for h from Equation 5.90 into Equation 5.89, the mass flux term for loss from the source zone by leaching (when no NAPL phase is present) is given by

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\frac{q_w M_i}{\theta_w R_i (z_b - z)} \tag{5.91}$$

for all times when a clean layer of soil exists above the source zone (i.e., when z > (S+E)t), and is given by

$$\left[\frac{dM_i}{dt}\right]_{leach} = -\frac{q_w M_i}{\theta_w R_i (z_b - (S+E)t)} \tag{5.92}$$

for all times when a clean layer of soil does not exist above the source zone (i.e., when $z \leq (S+E)t$).

For scenarios where an ISV remediation methodology has been implemented, the leaching term could still be given by the expression in Equation 5.64. However, as stated previously, expressions for the actual surface area and volume of the dissolving cracked glass as functions of time would be difficult to obtain in most instances. For ISV scenarios, wind suspension, water erosion, and volatilization mass fluxes are assumed to be zero because of the nature of the cracked glass waste form. This means that decay is the only other loss process occurring besides leaching. Therefore, the overall total concentration of a contaminant in the glass can be expressed as

$$C_{Ti} = \frac{M_{io} / e^{-\lambda_i t}}{V_{go}} \tag{5.93}$$

If we make the same idealizing assumption that was made when deriving Equation 5.66, the mass flux term for loss from the source zone by leaching for an ISV waste form is given by

$$\left[\frac{dM_i}{dt}\right]_{leach} = - \frac{r_g A_{sgo} M_{io} / e^{-\lambda_i t}}{\rho_g V_{go}} \tag{5.94}$$

For scenarios where an ISS remediation methodology has been implemented, wind suspension, water erosion, and volatilization mass fluxes are assumed to be zero because of the nature of the ISS waste form. This is a good assumption for wind suspension and water erosion because the grouting of the source zone into a solid waste form prevents soil particles from being removed by these processes. However, in reality volatilization could still occur by outward diffusion through the grout, and then upward diffusion through a clean layer of soil, if one is present. Simulating volatilization in this scenario would require some type of coupled, two-region diffusion theory. It would also require some kind of conceptualization of how downwardly percolating vadose zone water impinging on the upper face of the waste form (i.e., the boundary between the two regions) and being channeled around the waste form, affects boundary conditions of the mathematical problem at the interface. Such theory for volatilization was not developed for the current version of the source-term release module.

Recall that the conceptual model for leaching from an ISS waste form consists of diffusive movement of contaminants within the waste form to the outer boundary of the waste form, where they are lost to the vadose zone water that percolates past the faces of the waste form. The vadose zone water is assumed to move past the waste form fast enough that a zero concentration boundary condition applies for all contaminants at the faces of the waste form. The conceptualization leads to theory that predicts transient-state spatial gradients in concentration within the waste form. For any contaminant, *i*, the expression for mass flux out of the waste form developed from this theory (Equation 5.67 for the case where leaching is the only loss process) depends on the mass of contaminant *i* present in the waste form at the initial time (which was assumed to be spatially uniformly distributed within the waste for at that time). If contaminant *i* also undergoes decay/degradation, this same type of theoretical development can be used to obtain a similar expression for leaching loss mass flux (as a function of time) that accounts for the interaction of the decay/degradation process. Specifically, for all contaminants that are initially present in the source zone, the mass flux term for loss from the source zone by leaching (when decay/degradation also occurs) for an ISS waste form is given by

$$\left[\frac{dM_{i,1}}{dt}\right]_{leach} = -\,(M_{io'',1})\, e^{-\lambda_{i,1} t}\left(\frac{A_s}{V}\right)\sqrt{\frac{D_{gi,1}}{\pi\, t}} \tag{5.95}$$

where $M_{i,p}$ is the total mass or activity of the *p*-th member of the decay/degradation chain that starts with contaminant *i* (g or Ci)

$\lambda_{i,k}$ is the first-order decay/degradation coefficient for the *k*-th member of the decay/degradation chain that starts with contaminant *i* (yr^{-1}).

Note that for clarity later in the theoretical development, we have added an additional index to the subscripts of variables that depend on the particular contaminant species. The specific value '1' used for the second subscript indices p and k in Equation 5.95 denotes that this particular contaminant, *i*, was present in the source zone at the initial time (i.e., contaminant *i* is considered to be the first member of a possible decay/degradation chain of contaminants of concern). The quantity $M_{io'',1}$ is the initial mass of contaminant *i* in the source zone. The quantity $M_{i,1}$ is the mass of contaminant *i* in the source zone at time t that originated from $M_{io'',1}$, but that has been reduced from the value $M_{io'',1}$ because of decay/degradation. The quantities $\lambda_{i,1}$ and $D_{gi,1}$ are merely the first-order decay coefficient and effective diffusion coefficient in the waste form, respectively, for contaminant *i*. However, the added subscript index denotes that these are for a "parent" compound in a possible decay/degradation chain. Note also that Equation 5.95 is similar to Equation 5.67, except that an exponential decay factory for each contaminant initially present has been included. This factor, multiplied by the initial mass of the contaminant, is an expression of how the mass of contaminant *i* would have changed over time if no leaching loss would have occurred.

If every contaminant *i* merely decayed/degraded into a nontoxic compound that was not of concern, Equation 5.95 is all that would be needed to predict the leaching of each contaminant of concern. However, if a contaminant initially present in the source zone decays/degrades into another contaminant, Equation 5.95 cannot account for this additional progeny mass during the simulation because only the initial mass (rather than the actual mass as time t) appears in the equation. In other words, there is no simple way to add contaminant mass back into the calculations for subsequent times (as we do with the solution of equations for other scenarios). One might be tempted to use the same type of equation as Equation 5.95, only reset the initial mass variable to the added mass, and reset the time variable to make t = 0 coincide with the time of production of the new mass. However, this is not a valid approach because the theory behind Equation 5.95 assumes that the mass is spatially uniformly distributed at the initial time, while what is really occurring in the source zone is that new mass is being produced nonuniformly over space because gradients in the contaminant that produced it already exist at time t.

The source-term release module accounts for the leaching of progeny contaminants in the following way. For each contaminant *i* that is initially present in the source zone (as a "parent" contaminant), the module uses a set of equations to calculate the leaching losses of all progeny contaminants that were derived from the initial mass of contaminant *i*. Specifically, for all contaminants that are progeny of contaminant *i*, the mass flux term for loss from the source zone by leaching (when decay/degradation also occurs) for an ISS waste form is given by

$$\left[\frac{dM_{i,p}}{dt}\right]_{leach} = -M_{io'',1}\left(\prod_{k=2}^{p}\lambda_{i,k}\right)\left[\sum_{k=1}^{p}\left(\frac{e^{-\lambda_{i,k}t}}{\prod_{\substack{r=1\\r\neq k}}^{i}(\lambda_{i,r}-\lambda_{i,k})}\right)\right]\left(\frac{A_s}{V}\right)\sqrt{\frac{D_{gi,1}}{\pi\ t}} \tag{5.96}$$

Note that this equation is not an exact solution to the coupled contaminant diffusion problem because all contaminants may have their own unique effective diffusion coefficient in the waste form. Rather, Equation 5.96 contains the implicit assumption that all progeny contaminants have the same effective diffusion coefficient as their parent contaminant. In Equation 5.96, the product of the first three factors on the right-hand side of the equation is an expression of how the masses of progeny of contaminant *i* would have changed over time if no leaching loss would have occurred (i.e, it is the mass versus time function predicted by the Bateman equation [Bateman 1910]).

Contaminants that are part of a decay/degradation chain of one of the contaminants present initially may actually be one of the initial contaminants, or may be the same as one of the contaminants in the decay/degradation chain of another initial contaminant. Therefore, after all of the mass fluxes denoted by Equations 5.95 and 5.96 are calculated, the ones that correspond to the same contaminant are added together to produce one set of leaching mass flux terms (i.e., this summation procedure is how the module accounts for the accumulation and subsequent loss of daughter products).

When the soil is contaminated all the way up to the surface, the mass flux terms for loss from the source zone by wind suspension or water erosion are given by

$$\left[\frac{dM_i}{dt}\right]_{susp} = -\frac{S\,M_i}{z_b-(S+E)\,t} \tag{5.97}$$

$$\left[\frac{dM_i}{dt}\right]_{eros} = -\frac{E\,M_i}{z_b-(S+E)t} \tag{5.98}$$

Note that Equations 5.97 and 5.98 are similar to the expressions in Equations 5.71 and 5.72 for individual loss pathways, except for the fact that the thickness of the source zone must now be expressed as a function of both of these particle loss processes. When there is a clean layer of soil at the surface, the mass flux terms for wind suspension and water erosion are zero.

The appropriate mass flux terms for volatilization in scenarios where multiple contaminant loss processes are occurring concurrently were developed as follows. As was described above for the calculation of leaching loss mass flux terms, there may or may not be a clean layer present at any given time (depending on the relative rates of wind suspension, water erosion, and volatilization). When a clean layer is present, the mass flux term for contaminant loss from the source zone by volatilization is given by

$$\left[\frac{dM_i}{dt}\right]_{vol} = - \frac{A\,D_{vi}\,C_{vi}}{z - (S + E)t} \tag{5.99}$$

Note that Equation 5.99 is similar to Equation 5.73 (for the case where loss is by volatilization alone), except that the length of the diffusion path also depends on how much soil has been removed from the surface by wind suspension and water erosion. When a NAPL phase exists in the source zone, the vapor concentration in Equation 5.99 is calculated by the phase partitioning theory described in Section 2.2.4. When no NAPL phase exists in the source zone, C_{vi}, can be calculated by a simple phase partitioning relation, and the mass flux term is given by

$$\left[\frac{dM_i}{dt}\right]_{vol} = - \frac{D_{vi}\,K_{Hi}\,M_i}{\theta_w R_i (z_b - z)(z - (S + E)t)} \tag{5.100}$$

When a clean layer is not present, or when it is so thin that Equation 5.99 would predict unreasonably high values, the mass flux term for volatilization at that time is again taken to be the bounding value calculated by Equation 5.86.

Mass balance arguments (similar to those invoked when volatilization was the only process occurring) lead to the equation used by the module to compute the rate of recession of the upper boundary of the source zone, based on an individual contaminant, when a bounding value is not used for the volatilization flux term:

$$\frac{dz}{dt} = \frac{A\,D_{vi}\,C_{vi}\,(z_b - z)}{M_i (z - (S + E)\,t)} \tag{5.101}$$

When a NAPL phase exists in the source zone, the vapor concentration in Equation 5.101 is calculated by the phase partitioning theory described in Section 2.2.4. When no NAPL phase exists in the source zone, C_{vi}, can be calculated by a simple phase partitioning relation, and the rate of recession of the top boundary of the source zone, based on an individual contaminant, is given by

$$\frac{dz}{dt} = \frac{D_{vi}\,K_{Hi}}{\theta_w R_i (z - (S + E)t)} \tag{5.102}$$

When a bounding value is used for volatilization flux, the rate of recession of the top boundary of the source zone, based on an individual contaminant, is still given by Equation 5.87. As in the case where volatilization was the only loss process occurring, for contaminants that are components of the NAPL phase, Equation 5.80 is then used to calculate a single updated position of the top boundary of the source zone for all of the NAPL-phase components.

As a final note, recall that the source-term release module tests to determine if a NAPL phase exists at the beginning of each time step. Based on the specific theory presented in this section for the contaminated vadose zone source zone, Equation 2.1 can be rewritten as

$$M_i - (\theta_w C_{wi}^{sol} + \theta_a C_{vi}^{sat} + \beta_s K_{di} C_{wi}^{sol}) \cdot A \cdot (z_b - z) > 0 \qquad (5.103)$$

for all times when a clean layer exists and

$$M_i - (\theta_w C_{wi}^{sol} + \theta_a C_{vi}^{sat} + \beta_s K_{di} C_{wi}^{sol}) \cdot A \cdot (z_b - (S+E)t) > 0 \qquad (5.104)$$

for all times when a clean layer does not exist. Equations 5.103 and 5.104 are the test criteria that the module actually uses for contaminated vadose zone simulations.

5.6 Special Cases with Analytical Solutions

For scenarios where a) no NAPL phase is present, b) no volatilization occurs, c) no clean layer of soil exists above the source zone, d) no contaminant decays into another contaminant, and e) no remediation methodologies that must be described by unique theory are implemented, the resulting overall mass flux equation (i.e., Equation 5.56) has an analytical solution. The mass flux terms for decay/degradation, leaching, wind suspension, and water erosion are given by Equations 5.57, 5.92, 5.97, and 5.98, respectively. If these terms are substituted into Equation 5.56, the mass flux equation for this special case of multiple concurrent loss pathways is

$$\frac{dM_i}{dt} = -M_i \left(\lambda_i + \frac{q_w}{\theta_w R_i (z_b - (S+E)t)} + \frac{S}{z_b - (S+E)t} + \frac{E}{z_b - (S+E)t} \right) \qquad (5.105)$$

The analytical solution to Equation 5.105, assuming that the initial mass (at t = 0) of contaminant *i* is M_{io}, is

$$M_i(t) = M_{io} e^{-\lambda_i t} \cdot \left[\frac{z_b - (S+E)t}{z_b} \right]^{\left(\frac{\frac{q_w}{\theta_w R_i} + S + E}{S + E} \right)} \qquad (5.106)$$

This expression gives the total mass of a contaminant still within the source zone as a function time. Differentiating Equation 5.106 with respect to time (or substituting Equation 5.106 into Equation 5.105) gives

$$\frac{dM_i(t)}{dt} = -M_{io}\, e^{-\lambda_i t} \left(\frac{\frac{q_w}{\theta_w R_i} + S + E}{z_b - (S+E)t} + \lambda_i \right) \left[\frac{z_b - (S+E)t}{z_b} \right]^{\left(\frac{\frac{q_w}{\theta_w R_i} + S + E}{S + E} \right)} \tag{5.107}$$

which is an expression for the total mass flux lost from the source zone as a function of time. Equation 5.106 could be substituted into Equations 5.57, 5.92, 5.97, and 5.98 to produce analytical expressions for the individual mass loss rates as well. Equations 5.57, 5.92, 5.97, 5.98, and 5.106 could then be used to verify the outputs of the source-term release module for these scenarios, if none of the contaminants decay/degrade into other species of concern (e.g., other contaminants in the initial source inventory). If they do, this set of analytical solutions will not capture the entire decay-chain behavior (as the numerical procedure will).

Simpler scenarios (i.e., ones in which only a subsets of these four mass loss processes are occurring) can be modeled by these same equations by simply allowing the parameters related to the absent processes to go to zero. This is just a straightforward task of substituting zero for λ_i, q_w, S, or E for all scenarios except ones where both wind suspension and surface water erosion are absent. In this case, setting S and E to zero would cause the exponent in Equations 5.106 and 5.107 to approach infinity; and so the proper procedure is to take the limit of the right-hand side of Equation 5.106 as S and E approach zero to obtain the following expression:

$$[M_i(t)]_{E \to 0, S \to 0} = M_{io} \exp\left[-\left(\lambda_i + \frac{q_w}{\theta_w R_i z_b} \right) t \right] \tag{5.108}$$

When S and E are both zero, the total mass flux lost from the source zone as a function of time can be calculated by differentiating Equation 5.108 with respect to time to obtain

$$\left[\frac{M_i(t)}{dt} \right]_{E \to 0, S \to 0} = -M_{io} \left(\lambda_i + \frac{q_w}{\theta_w R_i z_b} \right) \exp\left[-\left(\lambda_i + \frac{q_w}{\theta_w R_i z_b} \right) t \right] \tag{5.109}$$

Closed-form expressions for the mass fluxes to each loss pathway (for this special case) can be obtained by substituting Equation 5.109 into Equations 5.57 and 5.92.

5.7 Numerical Solution Procedure for the General Case

In the general case of multiple, concurrent, contaminant loss pathways, an analytical solution to Equation 5.56 is not possible. Some of the reasons for this are the same as those discussed for the contaminated aquifer and contaminated pond source zones (i.e., complex NAPL partitioning theory, time varying parameters). When a NAPL phase is present in the source zone, the leaching term cannot be expressed as a single, simple function of M_i and t. Furthermore, even when a NAPL phase is not present, a number of system parameters may be arbitrary functions of time. In the case of the contaminated vadose zone source zone, the parameters that may be varying in time (due to natural phenomenon or the implementation of remediation methodologies) include the Darcy water flux density, wind suspension rate, and water erosion rate. The user has the ability to enter these parameters as a time series of discrete values. There are no hard limits on the number of elements constituting the time series used to describe such parameters. The code will allocate available memory as it is needed. Therefore, any arbitrary Darcy water flux density, wind suspension rate, or water erosion rate can be accommodated, provide memory and run time limits are not exceeded. In addition, when the volatilization loss route is included, the mathematical problem consists of simultaneously solving a set of coupled differential equations (rather than just one differential equation in M_i): one set of equations for the masses of each contaminant (e.g., Equation 5.99), plus one more for the position of the top boundary of the source zone (e.g., Equation 5.101).

In other words, the mathematical problem actually consists of the simultaneous numerical solution of a set of first-order, ordinary differential equations of the following form:

$$\frac{dM_i}{dt} = f_1(M_i,z,t) + f_2(M_i,z,t) + f_3(M_i,z,t) + f_4(M_i,z,t) = f(M_i,z,t) \quad i=1 \rightarrow n_c \qquad (5.110)$$

$$\frac{dz}{dt} = g(M_1, M_2, \ldots, M_{n_c}, z, t) \qquad (5.111)$$

where $f_1(\bullet)$, $f_2(\bullet)$, $f_3(\bullet)$, $f_4(\bullet)$, $f(\bullet)$, and $g(\bullet)$ are generic representations of functions of the variables $M_i(t)$, $z(t)$, and t. Furthermore, each of the four individual functions, $f_1(\bullet)$, $f_2(\bullet)$, $f_3(\bullet)$, and $f_4(\bullet)$, in Equation 5.110 represent one of the individual mass loss flux terms. Note that in reality, the function $f(\bullet)$ in the specific Equation 5.110 that corresponds to contaminant *i* might only depend on the mass M_i, and not the other masses. However, in general it can be said that $f(\bullet)$ is a function of all of the masses, z, and t (and that the functional dependence on masses other than M_i is nil). Therefore, Equations 5.110 and 5.111 truly can be described as a set of n_c+1 first-order, ordinary differential equations in n_c+1 unknowns.

The source-term release module solves this set of first-order, ordinary differential equations numerically by using a fourth-order Runge-Kutta method. This method requires four computations of the function $f(\bullet)$ or $g(\bullet)$ for each time step. The numerical algorithm begins at time $t = 0$ with $M_i = M_{io}$, and $z = z_t$. The value of z is updated first, using Equation 5.111 and assuming that the values of M_i for all the contaminants are held constant at their values at the beginning of the time step. Then each of the values of M_i are updated, using an equation like Equation 5.110 for each contaminant and assuming that the value of z is held constant at its value at the beginning of the time step.

The Runge-Kutta algorithm for updating the position of the top boundary of the source zone over the course of a time step is given by

$$z(t_{n+1}) = z(t_n) + \frac{1}{6}\left(k_1 + 2k_2 + 2k_3 + k_4\right) \tag{5.112}$$

where the terms in Equation 5.112 are given by

$$k_1 = \Delta t\, g(M_i(t_n), z(t_n), t_n) \tag{5.113}$$

$$k_2 = \Delta t\, g\left(M_i(t_n), z(t_n) + \frac{k_1}{2}, t_n + \frac{\Delta t}{2}\right) \tag{5.114}$$

$$k_3 = \Delta t\, g\left(M_i(t_n), z(t_n) + \frac{k_2}{2}, t_n + \frac{\Delta t}{2}\right) \tag{5.115}$$

$$k_4 = \Delta t\, g(M_i(t_n), z(t_n) + k_3, t_n + \Delta t) \tag{5.116}$$

(In the above equations, $M_i(t_n)$ and $z(t_n)$ are the values of M_i and z, respectively, at the time $n\Delta t$; and t_n is the time $n\Delta t$.) As long as a clean layer exists above the source zone, this numerical solution of Equation 5.111 is the appropriate way to update the value of z over the course of the time step. However, if wind suspension and water erosion would have caused the soil surface to recede to a depth deeper than this calculated value of z (from volatilization loss considerations) over the course of the time step, then z must be updated according to wind suspension and water erosion considerations. In other words, the value of z calculated from solution of Equation 5.111 must be compared to (S+E)t. If (S+E)t is the greater of these two quantities, the updated value of z is reset equal to (S+E)t.

The Runge-Kutta algorithm for updating contaminant masses over the course of a time step is given by

$$M_i(t_{n+1}) = M_i(t_n) + \frac{1}{6}\left(k_1 + 2k_2 + 2k_3 + k_4\right) \tag{5.117}$$

where the terms in Equation 5.117 are given by

$$k_1 = \Delta t\ f(M_i(t_n), z(t_n), t_n) \tag{5.118}$$

$$k_2 = \Delta t\ f\left(M_i(t_n) + \frac{k_1}{2}, z(t_n), t_n + \Delta\frac{t}{2}\right) \tag{5.119}$$

$$k_3 = \Delta t \, f\left(M_i(t_n) + \frac{k_2}{2}, z(t_n), t_n + \Delta\frac{t}{2} \right) \tag{5.120}$$

$$k_4 = \Delta t \, f(M_i(t_n) + k_3, z(t_n), t_n + \Delta t) \tag{5.121}$$

Note that because the function $f(\bullet)$ can be expressed as the sum of the functions $f_1(\bullet)$, $f_2(\bullet)$, $f_3(\bullet)$, and $f_4(\bullet)$ (from Equation 5.110), the Runge-Kutta procedure used to update the total contaminant mass in the source zone (described in Equations 5.117 through 5.121) contains calculations of the k_1 through k_4 terms that would be associated with the individual functions $f_1(\bullet)$, $f_2(\bullet)$, $f_3(\bullet)$, and $f_4(\bullet)$. Because these functions are associated with the individual mass loss terms, the numerical scheme allows us to also obtain the individual mass fluxes to each loss route at discrete times with minimal extra computation. This entire procedure is repeated as long as not all of the contaminant mass has been depleted from the source zone.

5.8 Methods for Calculating Selected Parameters in the Mass Loss Expressions

The first order decay/degradation coefficient is related to radioactive decay and degradation. The RAAS and MEPAS databases contain decay half lives for radionuclides and degradation half-lives for some non-radioactive contaminants. If values of half lives are available, the decay coefficient is calculated by

$$\lambda_i = \frac{\ln(2)}{t_{\frac{1}{2}i}} \tag{5.122}$$

For all volatilization-related calculations, the module uses the modified Henry's Law constant (unitless). The Henry's Law constant is obtained from the contaminant database and multiplied to obtain the unitless version by

$$K_{Hi} = \frac{H_i}{R \cdot T} \tag{5.123}$$

The Darcy water flux density may be entered by the user or calculated by the module. The user-entered value can be a single value or a piecewise-constant time series (consisting of an initial value, subsequent values, and the times at which the flux changes to those subsequent values). The module will calculate a Darcy water flux density using monthly climatology data and surface soil data as described in Section 5.1. All the other parameters in the mass flux equations for the leaching pathway are input directly by the user.

For wind suspension, a value for the wind suspension soil removal rate, S, must be obtained. The user may enter a known constant rate, a known piecewise-constant time series (consisting of an initial value, subsequent values, and the times at which the flux changes to those subsequent values), or let the module calculate the rate. If the user does not enter any known rates, the module will calculate a rate using the methods discussed in Section 5.2.

For surface water erosion, a value for the water erosion soil removal rate, E, must be obtained. The user may enter a known constant rate, a known piecewise-constant time series (consisting of an initial value, subsequent values, and the times at which the flux changes to those subsequent values), or let the module calculate the rate. If the user does not enter any known rates, the module will calculate a sediment removal rate using the methods discussed in Section 5.3.

The effective vapor diffusion coefficient in soil is given by

$$D_{vi} = \frac{\theta_a^{\frac{10}{3}} \cdot D_{vi}^{air}}{\theta_t^2} \tag{5.124}$$

where D_{vi}^{air} is the vapor diffusion coefficient of contaminant *i* in air ($cm^2\ yr^{-1}$).

5.9 Using Known Fluxes

For the contaminated vadose zone case, the known flux capabilities of the module can be applied to leaching, water erosion, wind suspension, and volatilization. Known flux capabilities can be used in two ways for each pathway. The first way to use known fluxes for leaching would be to pass known leaching flux rates to the groundwater transport code. The second way would be to "turn leaching off", by inputting a known leaching flux of 0. The same is true for the water erosion, wind suspension pathway, and the volatilization pathway. The volatilization pathway offers an additional method for adjusting flux. An adjustment factor (called the volatization ratio) is multiplied by $[dM_i/dt]_{vol}$ to reduce the volatization flux. The overall treatment of mass loss in the source-term module does not change. The known leach rate replaces the calculated value for $[dM_i/dt]_{leach}$, the known water erosion rate replaces the calculated $[dM_i/dt]_{eros}$, the known wind suspension rate replaces the calculated $[dM_i/dt]_{susp}$, and the known volatilization rate replaces the calculated $[dM_i/dt]_{vol}$ in Equation 5.56. All other calculations are done identically to the calculated flux cases.

6.0 Summary and Plans for Further Development

A contaminant source-term release module has been developed for MEPAS. This report documents the implementation of this computer module for MEPAS Version 3.2 and RAAS Version 1.1. Contaminated aquifer, pond/surface impoundment, and vadose zone source zones can be analyzed. Contaminants can be present in aqueous, sorbed, vapor, or NAPL phases. The module calculates the simultaneous contaminant fluxes (as functions of time) to various loss routes (i.e., degradation/decay, leaching, wind suspension, water erosion, overland flow, and/or volatilization) in a manner that accounts for interactions between loss processes and conserves overall mass. The outputs of the source-term release module are linked as inputs to the environmental transport, and exposure/health impact modules of MEPAS.

The source-term release module can be used to simulate "baseline" scenarios as well as scenarios where certain remediation methodologies have been implemented at the site. Remediation methodologies that can be simulated include all methodologies that can be represented merely by changing the magnitude of certain model parameters, as well as ISV and ISS methodologies in the vadose zone (which use different theory implemented in the module).

Because a numerical solution scheme is used to solve the differential equations of contaminant loss versus time, certain environmental input parameters can be entered as time-varying quantities rather than being constrained to constants. Analytical solutions that apply to special cases are also presented in the report.

For certain simpler scenarios, the numerical solution algorithms implemented in the module have been verified through comparison with analytical solutions. Tests of the algorithms for calculating loss to different routes have been conducted through applications of the source-term module to specific problem scenarios. Additional testing is in progress.

The current version of the source-term release module represents a consolidation and significant augmentation of numerous source-term release capabilities that existed in different modules of previous versions of MEPAS. However, it does not represent the ultimate source-term release capability envisioned for this component. The current version contains a number of idealizing assumptions and limitations. The remainder of this section discusses these, and describes further development plans envisioned for the module.

The current version of the module associated with RAAS Version 1.1 limits the contaminants that can be analyzed to those that already exist in the associated RAAS contaminant property database. In the future, the module may be modified to allow the user to analyze contaminants not already in the database (without actually modifying the database). In this event, values of all relevant contaminant-specific properties would have to be supplied by the user. (The capability to edit the MEPAS database already exists.)

The current version of the module determines whether a contaminant is one that may partition into a NAPL phase by using the database value of the modified (unitless) Henry's Law constant as a test metric (i.e., NAPL phase contaminant if $K_{Hi} > 10^{-7}$). This method makes appropriate determinations in most instances; but does lead to errors in cases that include nonvolatile organic compounds (e.g., PCBs) or volatile radionuclides (e.g., tritium and iodine). In the future, the module may be modified to include a new method to make this determination, either using the database value of the octanol-water partition coefficient as a test metric or (preferably) using the chemical's category number from the chemical classification system currently built into the RAAS software.

The current version of the module uses a relatively complex, yet still simplified, method of determining aqueous and vapor concentrations for a contaminant (at each time step) in systems where a NAPL phase exists. In the future, the module may be modified to include a full phase distribution model for this calculation (at each time step), which means that all volumetric fluid contents (water, air, NAPL) will be recalculated simultaneously with the contaminant phase partitioning.

This report presents analytical solutions applicable to special cases; however, they are not currently implemented in the module. In the future, these analytical solutions may be implemented so that the user can directly verify or bypass numerical outputs of the module.

Idealized theory for volatilization from a pond/surface impoundment source zone has been implemented in the module to act as a bounding calculation for highly volatile compounds that tended to disappear too quickly (with the 1-yr time step commonly used in simulations). However, simulated volatilization rates for these compounds still seem high. In the future, the module may be modified to correct this situation by either adding a capability to vary the length of the time step automatically during a simulation based on limits on the amount of mass that can be lost during a time step, or by implementing improved models for volatilization for the pond/surface impoundment source zone.

Finally, previous versions of MEPAS included the capability to analyze additional types of volatilization scenarios beyond what are currently implemented in the module. In the future, the module may be augmented to address these scenarios as well. These scenarios are 1) a landfill without internal gas generation, 2) a landfill with internal gas generation, 3) an aqueous pond/surface impoundment that contains a layer of contaminated sediment at the bottom (which controls the volatilization loss), and 4) a surface spill of liquid that is a NAPL-phase mixture.

7.0 Notation

This section contains definitions of all the symbols used in the report, along with their associated units.

a	factor in the LS-factor equation	unitless
a_j	coefficient for Blaney-Criddle PET function for the *j*-th month	mm d^{-1}
A	horizontal cross-sectional area of the contaminant source zone	cm^2
A_{dist}	aggregate size distribution	mm
A_{loss}	average-annual soil loss	t ha^{-1} yr^{-1}
A_s	surface area of the external boundary of an ISS waste form	cm^2
A_{sg}	total surface area of cracked glass in an ISV waste form	cm^2
A_{sgo}	initial total surface area of cracked glass in an ISV waste form	cm^2
b_j	coefficient for Blaney-Criddle PET function for the *j*-th month	unitless
c_j	correction factor for the Penman method with correction factor for the *j*-th month	unitless
c_{sky}	mean sky cover for a 12-hr period (tenths)	unitless
$c_{sky(j)}$	mean sky cover for the *j*-th month obtained from the LCD (tenths)	unitless
c_{vk}	von Karman constant	unitless
C_{fact}	vegetative cover factor	unitless
C_{oi}	concentration of contaminant *i* in the NAPL phase	g cm^{-3} or Ci cm^{-3}
C_{si}	concentration of contaminant *i* in the sorbed phase	g g^{-1} or Ci g^{-1}
C_{ti}	overall total concentration of contaminant *i* in a bulk volume of source zone	g cm^{-3} or Ci cm^{-3}

C_{tio}	value of overall total concentration of contaminant *i* used at the beginnning of a time step in the bounding calculation for volatization	g cm^{-3} or Ci cm^{-3}
C_{vi}	concentration of contaminant *i* in the vapor phase	g cm^{-3} or Ci cm^{-3}
C_{vi}^{sat}	saturated vapor concentration of contaminant *i*	g cm^{-3} or Ci cm^{-3}
C_{wi}	concentration of contaminant *i* in the aqueous phase	g cm^{-3} or Ci cm^{-3}
C_{wi}^{sol}	aqueous solubility of contaminant *i*	g cm^{-3} or Ci cm^{-3}
d_{12rd}	12-hr snowmelt from radiation	cm
d_{24rn}	daily snowmelt during a rainfall event	cm
d_{6c}	6-hr snowmelt from convection	cm
d_{6vc}	6-hr snowmelt from vapor condensation	cm
d_{cj}	average monthly snowmelt from convection for the *j*-th month	cm
d_{fmax}	peak flow depth	cm
d_p	depth of the pond	cm
d_{pr}	daily precipitation depth	cm
d_{praj}	precipitation adjusted for snowmelt for the *j*-th month	cm
d_{pruj}	unadjusted precipitation depth for the *j*-th month obtained from the LCD	cm
d_{rdj}	average monthly snowmelt from radiation for the *j*-th month	cm
d_{rnj}	snowmelt from rainfall for the *j*-th month	cm
d_{roj}	overland runoff for the *j*-th month	cm
d_{sj}	total snowmelt for the *j*-th month	cm
d_{vcj}	average monthly snowmelt from vapor condensation for the *j*-th month	cm

D_{gi}	effective diffusion coefficient of contaminant i within an ISS waste form	cm^2 yr^{-1}
D_{vi}	effective vapor diffusion coefficient of contaminant i in soil	cm^2 yr^{-1}
D_{vi}^{air}	vapor diffusion coefficient of contaminant i in air	cm^2 yr^{-1}
e_a	actual vapor pressure of the air	mbar
e_{aj}	mean actual vapor pressure of the air for the j-th month	mbar
e_{sj}	saturation vapor pressure at mean air temperature for the j-th month	mbar
E	volumetric water erosion rate	cm yr^{-1}
E_{aj}	actual evapotranspiration for the j-th month	cm
E_{pj}	potential evapotranspiration rate for the j-th month	mm d^{-1}
E_{lim}	annual average limited emission rate per unit surface area	g yr^{-1}
E_{pav}	emission rate for traffic on paved roads	g vehicle^{-1} km^{-1}
E_{pot}	erosion potential	g m^{-2}
E_{road}	emission rate from road surfaces	g vehicle^{-1} km^{-1}
E_{unlim}	annual average unlimited emission rate per unit surface area	g yr^{-1}
E_{unpav}	emission rate for traffic on unpaved roads	g vehicle^{-1} km^{-1}
E_{veh}	emission rate for suspension due to vehicular travel	g yr^{-1}
E_{wind}	total emission rate for wind erosion	g yr^{-1}
E_{wm}	emission rate for wind/mechanical suspension	g yr^{-1}
f_{cr}	fraction of soil surface that is crusted	unitless
f_d	frequency of mechanical disturbances	month^{-1}
f_{hj}	factor for the j-th month to correct the wind speed measurement to a 2-m measurement height	unitless

f_j	coefficient for Blaney-Criddle PET function for the *j*-th month	mm day^{-1}
f_{ne}	nonerodible elements correction factor	unitless
f_p	particle size parameter	unitless
f_{PE}	Thornthwaite's Precipitation-Evaporation (PE) Index	unitless
f_{perm}	profile-permeability class factor	unitless
f_v	fraction of surface covered with vegetation	unitless
f_{wj}	temperature-related weighting factor for the *j*-th month	unitless
h	thickness of the contaminant source zone	cm
h_0	elevation of LCD station	m
h_1	elevation of actual site	m
$h^{rel}_{ave(j)}$	average percent relative humidity for the *j*-th month	unitless
h_m	wind speed measurement height above ground	m
$h^{rel}_{max(j)}$	maximum percent relative humidity for the *j*-th month	unitless
$h^{rel}_{min(j)}$	minimum percent relative humidity for the *j*-th month	unitless
h_{ref}	reference height above the soil surface	m
H_i	Henry's Law constant for contaminant *i* (press./concen. basis)	atm m^3 mol^{-1}
i	index on contaminant	unitless
I_j	leachate generation for the *j*-th month	cm
$I_{max(j)}$	maximum amount of moisture available for percolation in the *j*-th month	cm
$I_{pot(j)}$	potential percolation for the *j*-th month	cm
j	index on month	unitless

k	index on contaminants other than contaminant *i*	unitless
k_1 - k_4	the four intermediate terms in the Runge-Kutta calculations	---------
k_{ig}	gas-phase mass transfer coefficient for contaminant *i* at a pond surface	cm yr^{-1}
k_{il}	liquid-phase mass transfer coefficient for contaminant *i* at a pond surface	cm yr^{-1}
K_1	theoretical constant in equation for snowmelt by vapor condensation	cm s $mbar^{-1}$ m^{-1}
K_2	heat exchange coefficient as a function of elevation	cm s m^{-1} $°C^{-1}$
K_{di}	linear equilibrium sorption coefficient for contaminant *i* to a solid sorbent	cm^3 g^{-1}
K_{fact}	soil erodibility factor	t ha^{-1} yr^{-1} per unit R_{fact}
K_{Hi}	modified Henry's Law constant for contaminant *i* (concen./concen. basis) for partitioning between aqueous solution and vapor	unitless
K_{Hi}^{org}	modified "Henry's Law" constant for contaminant *i* (concen./concen. basis) for partitioning between NAPL and vapor	unitless
K_{li}	overall mass transfer coefficient from a liquid phase to the atmosphere for contaminant *i*, expressed in terms of the liquid-phase concentration	cm yr^{-1}
K_{owi}	octanol-water partition coefficient for contaminant *i*	unitless
K_{rd}	snowmelt occurring by radiation in a half-day in clear weather	cm
K_{rdj}	average snowmelt occurring by radiation in a half-day in clear weather for the *j*-th month	cm
K_{wi}^{org}	analogue of the modified "Henry's Law" constant for contaminant *i* for partitioning between NAPL and aqueous phases	unitless
L_r	surface roughness length	m
L_{road}	distance of travel over contaminated surface	km

L_{slope}	slope length	cm
L_x	dimension of the contaminated aquifer source zone parallel to flow	cm
L_y	horizontal dimension of the contaminated aquifer source zone perpendicular to flow	cm
L_z	vertical dimension of the contaminated aquifer source zone perpendicular to flow	cm
m_{LS}	exponent in the LS-factor equation	unitless
M_i	total mass or activity of contaminant *i* in the source zone	g or Ci
M_{io}	initial total mass or activity of contaminant *i* in the source zone	g or Ci
$M_{io'}$	total mass or activity of contaminant *i* in the source zone at the time the zone was subjected to ISV remediation	g or Ci
$M_{io''}$	total mass or activity of contaminant *i* in the source zone at the time the zone was subjected to ISS remediation	g or Ci
$M_{i,p}$	total mass or activity of the *p*-th member of the decay/degradation chain that starts with contaminant *i*	g or Ci
M_{mi}	molecular weight of contaminant *i*	g mol^{-1}
M_{veh}	mean vehicle weight	Mg
n	time step index used in the Runge-Kutta equations	unitless
n_c	total number of contaminants in the source zone	unitless
n_{cn}	total number of constituents in the NAPL phase	unitless
n_{dj}	number of days in the *j*-th month	unitless
n_p	number of days with at least 0.254 mm (0.01 in.) of precipitation per year	unitless
n_{pj}	number of precipitation events during the *j*-th month	unitless

n_{scs}	SCS Curve Number used for runoff calculations	unitless
n_v	average number of vehicles traveling over the contaminated surface per day	vehicle d^{-1}
n_w	mean number of wheels on a vehicle	unitless
p_j	mean daily percentage of total annual daytime hours as a function of latitude for the *j*-th month	unitless
$P_{2,6}$	2-year recurrence interval, 6-hr duration rainfall depth	cm
P_{clay}	percent clay	unitless
P_{fact}	erosion control practice factor	unitless
P_{om}	percent organic matter	unitless
P_{sand}	percent sand	unitless
P_{silt}	percent silt plus very fine sand	unitless
q_w	Darcy flux density of water flowing through the aquifer or vadose zone	cm yr^{-1}
Q_{over}	total flux of aqueous solution, sediment, and NAPL globules as pond runoff	cm^3 yr^{-1}
Q_w	volumetric flux of water flowing through the aquifer source zone or vadose zone source zone, or out of the bottom of a pond/surface impoundment source zone	cm^3 yr^{-1}
r	index on contaminants other that contaminant *i*	unitless
r_g	mass dissolution rate of glass in an ISV waste form per surface area	g yr^{-1} cm^{-2}
$r_{sun(j)}$	ratio of actual to maximum possible sunshine hours for the *j*-th month	unitless
R	Universal gas constant	atm L mol^{-1} K^{-1}
R_{aj}	extraterrestrial radiation, in equivalent evaporation for the *j*-th month	mm d^{-1}

R_{fact}	rainfall erosivity factor	(100m) (t ha^{-1}) (cm yr^{-1})
R_i	retardation factor, or phase apportionment factor, for contaminant *i*	unitless
R_{nj}	net radiation, in equivalent evaporation, for the *j*-th month	mm d^{-1}
R_{nlj}	net longwave radiation, in equivalent evaporation, for the *j*-th month	mm d^{-1}
R_{nsj}	net shortwave radiation, in equivalent evaporation, for the *j*-th month	mm d^{-1}
R_{sj}	solar radiation, in equivalent evaporation, for the *j*-th month	mm d^{-1}
S	volumetric wind suspension rate	cm yr^{-1}
S_{fact}	slope length and steepness factor	unitless
$S_{m(j)}$	soil moisture storage for the *j*-th month	cm
S_{slope}	slope gradient (in percent)	unitless
S_{struc}	soil structure index	unitless
t	time since initial condition of the source zone	yr
$t_{1/2i}$	decay/degradation half life of contaminant *i* in any phase	yr
t_n	value of time equal to $n\Delta t$	yr
T	absolute temperature	K
T_{12}	average 12-hr temperature	°C
T_{24}	average daily air temperature	°C
T_6	average 6-hr temperature	°C
T_{aj}	adjusted average monthly temperature at the actual site for the *j*-th month	°C
T_{uj}	unadjusted average monthly temperature at the LCD station for the *j*-th month	°C

$\overline{U}$	average wind speed	m s^{-1}
$U_{6,15}$	average 6-hr wind velocity measured at 15 m (50 ft) above the ground	m s^{-1}
U_c	critical wind speed at the reference height above the soil surface	m s^{-1}
U_{d2j}	mean monthly daytime wind speed at a 2-m height for the *j*-th month	m s^{-1}
U_f	threshold friction velocity	m s^{-1}
$\overline{U}_j$	average wind speed for the *j*-th month , obtained from the LCD	m s^{-1}
U_{max}	maximum wind speed at a reference height above the soil surface	m s^{-1}
$\overline{U}_y$	mean annual wind speed	m s^{-1}
v_{veh}	mean vehicle speed	km hr^{-1}
V	overall volume of the contaminated source zone	cm^3
V_g	volume of cracked glass in an ISV waste form	cm^3
V_{go}	initial volume of cracked glass in an ISV waste form	cm^3
w_{pj}	accumulated potential water loss for the *j*-th month	cm
w_{WHC}	water-holding capacity of the soil	cm
X_{oi}	mole fraction of contaminant *i* in the NAPL phase	unitless
z	distance from the initial position of the soil surface to the top of the source zone at time t	cm
z_b	distance from the initial position of the soil surface to the bottom of the source zone at any time	cm
z_t	distance from the initial position of the soil surface to the initial position of the top of the source zone (i.e., initial thickness of clean layer)	cm
α	land surface reflectiveness correction parameter	unitless
ß	bulk density of the solid-sorbent phase	g cm^{-3}

β_s	soil bulk density for an aquifer or vadose zone	g cm^{-3}
β_{ss}	concentration of suspended sediment in the pond water	g cm^{-3}
Δt	time step size in Runge-Kutta calculations	yr
λ_i	first-order decay/degradation coefficient for contaminant *i*	yr^{-1}
$\lambda_{i,k}$	first-order decay/degradation coefficient for the *k*-th member of the decay/degradation chain that starts with contaminant *i*	yr^{-1}
ρ_g	density of glass in an ISV waste form	g cm^{-3}
ρ_{li}	density of contaminant *i* in the pure liquid form	g cm^{-3}
σ	constant in the estimation equation for R_{nlj}	unitless
θ_a	volumetric air content of the soil	unitless (cm^3 cm^{-3})
θ_w	volumetric water content of the soil	unitless (cm^3 cm^{-3})
θ_t	total porosity of the soil	unitless (cm^3 cm^{-3})

8.0 References

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Appendix A

Complete List of Source-Term Module Input Parameters

Appendix A

Complete List of Source-Term Module Input Parameters

The following tables list the computer code variable names for input parameters for the source-term module. They also show the relationship of those variables to the variables presented in the main body of the report. Note that there is not a direct one-to-one mapping of code variable names to variables presented in the report. For example, one computer code variable may represent one of a number of similar report equation variables, depending on which type of contamination scenario is being simulated. Furthermore, sometimes a computer code variable is input with a certain (more commonly available) set of units, and then the code converts the value to the set of units used in the report equations.

Table A.1. Site Constant Parameters

Name	Units	Description	Notation
SFDBULKD	g cm^{-3}	Dry bulk density of surface soil	β_s
STAREA	cm^2	Area of the waste site	A
STAVAILW	cm	Water-holding capacity of waste zone	w_{WHC}
STAVTEMP	°C	Average air temperature at the waste site	T_{24}
STAVWINDV	m s^{-1}	Mean annual wind speed	$\overline{U}$
STCFACTR	--	Vegetative cover factor	f_v
STCLOUD	fraction	Fraction of sky with cloud cover	c_{sky}
STCORRSC	--	Non-erodible area correction factor	f_{ne}
STCRUST	fraction	Fraction of surface area covered with a crust layer	f_{cr}
STDELTA_T	yr	Length of time step	Δt
STELEV	m	Elevation of waste site	h_1
STKFACTR	English Units[a]	Soil erodibility factor	K_{fact}
STLAT	degrees	Latitude of waste site	--
STLCDELEV	m	Elevation of Local Climatalogical Data (LCD) Station	h_0
STLENGTH	cm	Length of site down erodible slope	L_{slope}

---

[a] English ton $acre^{-1}$ yr^{-1} per unit R_{fact} in English units.

Table A.1. (contd)

Name	Units	Description	Notation
STLOCSUR	m	Surface roughness length	L_r
STMAXTIME	yr	Length of run	--
STMAXWIND	$m\ s^{-1}$	Maximum wind speed at site	U_{max}
STMINWST	--	The minimum waste fraction for which analysis performed	--
STMNUMPRE	--	Number of monthly precipitation events	n_{pj}
STMOISTC	fraction	The volumetric moisture content fraction of the source zone	θ_w
STMPRECIP	cm	Monthly precipitation amount measured at LCD	d_{pruj}
STNUMDIS	$month^{-1}$	Frequency of mechanical disturbances to site	f_d
STNUMPRCP	yr^{-1}	Number of days with >0.254mm precipitation	n_p
STOVLFLX	fraction	Overland flux for a ponded case as fraction of total water volume.	$\frac{Q_{over}\,t}{A\,d_p}$
STPEI	--	Thornthwaite's Precipitation-Evaporation Index	f_{PE}
STPFACTR	--	Erosion control practice factor	P_{fact}
STPRECIP	cm	2-yr, 6-hr, precipitation event	$P_{2,6}$
STRHMAX	%	Maximum monthly relative humidity	$h^{rel}_{max(j)}$
STRHMIN	%	Minimum monthly relative humidity	$h^{rel}_{min(j)}$
STROADS	--	Flag to designate type of road travel	Control
STRTDIST	km	Distance traveled over contaminated surface	L_{road}
STRTNUM	day^{-1}	Average number of vehicles traveling over surface daily	n_v
STSAND	%	Percent sand in surface soil	P_{sand}
STSCSCN	--	SCS curve number	n_{scs}
STSILT	%	Percent of silt on road surface	P_{silt}
STSLOPE	%	Slope of waste site	S_{slope}

Table A.1. (contd)

Name	Units	Description	Notation
STSSOL	g cm^{-3}	Concentration of suspended solids in surface impoundment	β_{ss}
STSTORMI	--	Storm type index for location of waste site	--
STTEMP	°C	Temperature measured at LCD	T_{24}
STTHICK	cm	Thickness of the waste zone	h, L_x, d_p
STVEGFR	fraction	Fraction of surface area covered with vegetation	f_v
STVSPEED	km hr^{-1}	Mean vehicle speed at site	v_{veh}
STVWEIGH	Mg	Mean vehicle weight	M_{veh}
STWHEELS	--	Mean number of wheels per vehicle	n_w
STWINDHT	m	Height above ground of local wind measurements	h_{in}
STWINDV	m s^{-1}	Mean monthly wind speed at LCD	U_{d2}
WZDBULKD	g cm^{-3}	Dry bulk density of waste zone	β_s

Table A.2. Site Series Parameters

Name	Units	Description	Notation
STAIRSPC	fraction	The volumetric air content fraction of the source zone	θ_a
STAIRSPC_TIM	yr	Times for air space-time pairs	t
STAIRSPC_NUM	--	This is the number of different airspace percentages	Counter
STCLEAN	cm	The initial thickness of the clean layer	z_t
STCLEAN_TIM	yr	Times for cover thickness-time pairs	t
STCLEAN_NUM	--	This is the number of different clean layer thicknesses	Counter
STDARCY	cm yr^{-1}	Darcy infiltration rate	q_w
STDARCY_TIM	yr	Times for infiltration-time pairs	t
STDARCY_NUM	--	This is the number of different infiltration rates	Counter
STTOTPOR	fraction	The total porosity fraction of the source zone	θ_t
STTOTPOR_TIME	yr	Times for porosity-time pairs	t
STTOTPOR_NUM	--	This is the number of different total porosity percentages	Counter
STWATR	cm yr^{-1}	Water erosion rate	E
STWATR_TIM	yr	Times for water erosion-time pairs	t
STWATR_NUM	--	This is the number of different water erosion rates	Counter
STWIND	cm yr^{-1}	Wind erosion rate	S
STWIND_TIM	yr	Times for wind erosion-time pairs	t
STWIND_NUM	--	This is the number of different wind erosion rates	Counter

Table A.3. Contaminant Constant Parameters

Name	Units	Description	Notation
CLDIFCO	$cm^2\ yr^{-1}$	Grout Diffusion Coefficient for each contaminant	D_g
CLHLC	$\frac{atm\ m^3}{mol}$	Henry's Law Constant for each contaminant	H
CLKOW	$mL\ g^{-1}$	Octanol-water partitioning coefficient for each contaminant	K_{ow}
CLKTYPE	--	Contaminant type for each contaminant	Database Param
CLLAMBDA	yr^{-1}	Decay/degradation constant for each contaminant	λ
CLSPECACT	$Ci\ g^{-1}$	Specific activity for each contaminant	Database Param
CLVAP	mm Hg	Vapor Pressure for each contaminant	C_v^{sat}
CLWM	$g\ mol^{-1}$	Molecular weight for each contaminant	M_m
FSCASID	--	CAS ID for each contaminant	Database Param
NDS	--	Number of daughter products for each contaminant	Database Param
NUMALLCON	--	Number of all contaminants (parents plus progeny)	n_c
NUMCON	--	Number of contaminants (parents only)	n_c
STINVEN	g	Inventory quantity for each contaminant	M_{io}
STORGCON	$g\ cm^{-3}$	Concentration of organic contaminants in the organic phase	C_o
STSOL	$g\ mL^{-1}$	Aqueous solubility for each contaminant	C_w^{sol}
STVOLRAT	fraction	Volatilization ratio used for control of volatilization	--

Table A.4. Contaminant Series Parameters

Name	Units	Description	Notation
STKD	mL g^{-1}	K_d for each contaminant	K_d
STKD_TIM	yr	Time for K_d-time series	t
STKD_NUM	--	Number of different K_d values used	Counter

Table A.5. Waste Form Series Parameters

Name	Units	Description	Notation
STGLASS	yr^{-1}	Glass dissolution rate	r_g
STGLASS_TIM	yr	Times for dissolution-time series	t
STGLASS_NUM	--	This is the number of different glass dissolution rates	Counter
STSURFVOL	cm^{-1}	Surface to volume ratio of the grout monolith	A_{sg}/V_g
STSURFVOL_TIM	yr	Times for surface/volume-time series	t
STSURFVOL_NUM	--	This is the number of different monolith surface to volume ratios	Counter

Table A.6. Pathway Series Parameters

Name	Units	Description	Notation
STLEACH	$g\ yr^{-1}$	Known leaching flux rates	$\left[\frac{dM}{dt}\right]_{leach}$
STLEACH_TIM	yr	Times for flux-time leaching series	t
STLEACH_NUM	--	Number of known leach loss flux rates	Counter
STOVL	$g\ yr^{-1}$	Known overland flux rates	$\left[\frac{dM}{dt}\right]_{over}$ $\left[\frac{dM}{dt}\right]_{eros}$
STOVL_TIM	yr	Times for flux-time overland series	t
STOVL_NUM	--	Number of known overland flux rates	Counter
STSUSP	$g\ yr^{-1}$	Known wind suspension flux rates	$\left[\frac{dM}{dt}\right]_{susp}$
STSUSP_TIM	yr	Times for flux-time suspension series	t
STSUSP_NUM	--	Number of known suspension flux rates	Counter
STVOLAT	$g\ yr^{-1}$	Known volatilization flux rates	$\left[\frac{dM}{dt}\right]_{vol}$
STVOLAT_TIM	yr	Times for flux-time volatilization series	t
STVOLAT_NUM	--	Number of different volatilization rates	Counter
STSOURCE	$g\ yr^{-1}$	Known flux rates for a source to the waste zone	$\left[\frac{dM}{dt}\right]_{source}$
STSOURCE_TIM	yr	Times for flux-time source series	t
STSOURCE_NUM	--	Number of different flux rates for a source to the waste zone	Counter

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