HMCRP

REPORT 2

HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

Sponsored by the Pipeline and Hazardous Materials Safety Administration

Assessing Soil and Groundwater Impacts of Chemical Mixture Releases from Hazardous Materials Transportation Incidents

TRANSPORTATION RESEARCH BOARD
OF THE NATIONAL ACADEMIES

TRANSPORTATION RESEARCH BOARD 2010 EXECUTIVE COMMITTEE*

OFFICERS

CHAIR: **Michael R. Morris,** *Director of Transportation, North Central Texas Council of Governments, Arlington*
VICE CHAIR: **Neil J. Pedersen,** *Administrator, Maryland State Highway Administration, Baltimore*
EXECUTIVE DIRECTOR: **Robert E. Skinner, Jr.,** *Transportation Research Board*

MEMBERS

J. Barry Barker, *Executive Director, Transit Authority of River City, Louisville, KY*
Allen D. Biehler, *Secretary, Pennsylvania DOT, Harrisburg*
Larry L. Brown, Sr., *Executive Director, Mississippi DOT, Jackson*
Deborah H. Butler, *Executive Vice President, Planning, and CIO, Norfolk Southern Corporation, Norfolk, VA*
William A.V. Clark, *Professor, Department of Geography, University of California, Los Angeles*
Eugene A. Conti, Jr., *Secretary of Transportation, North Carolina DOT, Raleigh*
Nicholas J. Garber, *Henry L. Kinnier Professor, Department of Civil Engineering, and Director, Center for Transportation Studies, University of Virginia, Charlottesville*
Jeffrey W. Hamiel, *Executive Director, Metropolitan Airports Commission, Minneapolis, MN*
Paula J. Hammond, *Secretary, Washington State DOT, Olympia*
Edward A. (Ned) Helme, *President, Center for Clean Air Policy, Washington, DC*
Adib K. Kanafani, *Cahill Professor of Civil Engineering, University of California, Berkeley*
Susan Martinovich, *Director, Nevada DOT, Carson City*
Debra L. Miller, *Secretary, Kansas DOT, Topeka*
Sandra Rosenbloom, *Professor of Planning, University of Arizona, Tucson*
Tracy L. Rosser, *Vice President, Corporate Traffic, Wal-Mart Stores, Inc., Mandeville, LA*
Steven T. Scalzo, *Chief Operating Officer, Marine Resources Group, Seattle, WA*
Henry G. (Gerry) Schwartz, Jr., *Chairman (retired), Jacobs/Sverdrup Civil, Inc., St. Louis, MO*
Beverly A. Scott, *General Manager and Chief Executive Officer, Metropolitan Atlanta Rapid Transit Authority, Atlanta, GA*
David Seltzer, *Principal, Mercator Advisors LLC, Philadelphia, PA*
Daniel Sperling, *Professor of Civil Engineering and Environmental Science and Policy; Director, Institute of Transportation Studies; and Interim Director, Energy Efficiency Center, University of California, Davis*
Kirk T. Steudle, *Director, Michigan DOT, Lansing*
Douglas W. Stotlar, *President and CEO, Con-Way, Inc., Ann Arbor, MI*
C. Michael Walton, *Ernest H. Cockrell Centennial Chair in Engineering, University of Texas, Austin*

EX OFFICIO MEMBERS

Peter H. Appel, *Administrator, Research and Innovative Technology Administration, U.S.DOT*
J. Randolph Babbitt, *Administrator, Federal Aviation Administration, U.S.DOT*
Rebecca M. Brewster, *President and COO, American Transportation Research Institute, Smyrna, GA*
George Bugliarello, *President Emeritus and University Professor, Polytechnic Institute of New York University, Brooklyn; Foreign Secretary, National Academy of Engineering, Washington, DC*
Anne S. Ferro, *Administrator, Federal Motor Carrier Safety Administration, U.S.DOT*
LeRoy Gishi, *Chief, Division of Transportation, Bureau of Indian Affairs, U.S. Department of the Interior, Washington, DC*
Edward R. Hamberger, *President and CEO, Association of American Railroads, Washington, DC*
John C. Horsley, *Executive Director, American Association of State Highway and Transportation Officials, Washington, DC*
David T. Matsuda, *Deputy Administrator, Maritime Administration, U.S.DOT*
Victor M. Mendez, *Administrator, Federal Highway Administration, U.S.DOT*
William W. Millar, *President, American Public Transportation Association, Washington, DC*
Tara O'Toole, *Under Secretary for Science and Technology, U.S. Department of Homeland Security, Washington, DC*
Robert J. Papp (Adm., U.S. Coast Guard), *Commandant, U.S. Coast Guard, U.S. Department of Homeland Security, Washington, DC*
Cynthia L. Quarterman, *Administrator, Pipeline and Hazardous Materials Safety Administration, U.S.DOT*
Peter M. Rogoff, *Administrator, Federal Transit Administration, U.S.DOT*
David L. Strickland, *Administrator, National Highway Traffic Safety Administration, U.S.DOT*
Joseph C. Szabo, *Administrator, Federal Railroad Administration, U.S.DOT*
Polly Trottenberg, *Assistant Secretary for Transportation Policy, U.S.DOT*
Robert L. Van Antwerp (Lt. Gen., U.S. Army), *Chief of Engineers and Commanding General, U.S. Army Corps of Engineers, Washington, DC*

*Membership as of October 2010.

HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

HMCRP REPORT 2

Assessing Soil and Groundwater Impacts of Chemical Mixture Releases from Hazardous Materials Transportation Incidents

Richard G. Lewis
Ziqi He
HSA Engineers & Scientists
A Member of the Conestoga-Rovers & Associates
Family of Companies
Fort Myers, FL

Subscriber Categories
Highways • Motor Carriers • Railroads • Environment • Freight Transportation
Geotechnology • Hydraulics and Hydrology

Research sponsored by the Pipeline and Hazardous Materials Safety Administration

TRANSPORTATION RESEARCH BOARD

WASHINGTON, D.C.
2010
www.TRB.org

HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

The safety, security, and environmental concerns associated with transportation of hazardous materials are growing in number and complexity. Hazardous materials are substances that are flammable, explosive, or toxic or that, if released, produce effects that would threaten human safety, health, the environment, or property. Hazardous materials are moved throughout the country by all modes of freight transportation, including ships, trucks, trains, airplanes, and pipelines.

The private sector and a diverse mix of government agencies at all levels are responsible for controlling the transport of hazardous materials and for ensuring that hazardous cargoes move without incident. This shared goal has spurred the creation of several venues for organizations with related interests to work together in preventing and responding to hazardous materials incidents. The freight transportation and chemical industries; government regulatory and enforcement agencies at the federal and state levels; and local emergency planners and responders routinely share information, resources, and expertise. Nevertheless, there has been a long-standing gap in the system for conducting hazardous materials safety and security research. Industry organizations and government agencies have their own research programs to support their mission needs. Collaborative research to address shared problems takes place occasionally, but mostly occurs on an ad hoc basis.

Acknowledging this gap in 2004, the U.S. DOT Office of Hazardous Materials Safety, the Federal Motor Carrier Safety Administration, the Federal Railroad Administration, and the U.S. Coast Guard pooled their resources for a study. Under the auspices of the Transportation Research Board (TRB), the National Research Council of the National Academies appointed a committee to examine the feasibility of creating a cooperative research program for hazardous materials transportation, similar in concept to the National Cooperative Highway Research Program (NCHRP) and the Transit Cooperative Research Program (TCRP). The committee concluded, in *TRB Special Report 283: Cooperative Research for Hazardous Materials Transportation: Defining the Need, Converging on Solutions,* that the need for cooperative research in this field is significant and growing, and the committee recommended establishing an ongoing program of cooperative research. In 2005, based in part on the findings of that report, the Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (SAFETEA-LU) authorized the Pipeline and Hazardous Materials Safety Administration (PHMSA) to contract with the National Academy of Sciences to conduct the Hazardous Materials Cooperative Research Program (HMCRP). The HMCRP is intended to complement other U.S. DOT research programs as a stakeholder-driven, problem-solving program, researching real-world, day-to-day operational issues with near- to mid-term time frames.

HMCRP REPORT 2

Project HM-06
ISSN 2150-4849
ISBN: 978-0-309-15527-4
Library of Congress Control Number 2010941499

NOTICE

The project that is the subject of this report was a part of the Hazardous Materials Cooperative Research Program, conducted by the Transportation Research Board with the approval of the Governing Board of the National Research Council.

The members of the technical panel selected to monitor this project and to review this report were chosen for their special competencies and with regard for appropriate balance. The report was reviewed by the technical panel and accepted for publication according to procedures established and overseen by the Transportation Research Board and approved by the Governing Board of the National Research Council.

The opinions and conclusions expressed or implied in this report are those of the researchers who performed the research and are not necessarily those of the Transportation Research Board, the National Research Council, or the program sponsors.

The Transportation Research Board of the National Academies, the National Research Council, and the sponsors of the Hazardous Materials Cooperative Research Program do not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of the report.

Published reports of the

HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

are available from:

Transportation Research Board
Business Office
500 Fifth Street, NW
Washington, DC 20001

and can be ordered through the Internet at:

http://www.national-academies.org/trb/bookstore

Printed in the United States of America

THE NATIONAL ACADEMIES

Advisers to the Nation on Science, Engineering, and Medicine

The **National Academy of Sciences** is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. On the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Ralph J. Cicerone is president of the National Academy of Sciences.

The **National Academy of Engineering** was established in 1964, under the charter of the National Academy of Sciences, as a parallel organization of outstanding engineers. It is autonomous in its administration and in the selection of its members, sharing with the National Academy of Sciences the responsibility for advising the federal government. The National Academy of Engineering also sponsors engineering programs aimed at meeting national needs, encourages education and research, and recognizes the superior achievements of engineers. Dr. Charles M. Vest is president of the National Academy of Engineering.

The **Institute of Medicine** was established in 1970 by the National Academy of Sciences to secure the services of eminent members of appropriate professions in the examination of policy matters pertaining to the health of the public. The Institute acts under the responsibility given to the National Academy of Sciences by its congressional charter to be an adviser to the federal government and, on its own initiative, to identify issues of medical care, research, and education. Dr. Harvey V. Fineberg is president of the Institute of Medicine.

The **National Research Council** was organized by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and advising the federal government. Functioning in accordance with general policies determined by the Academy, the Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in providing services to the government, the public, and the scientific and engineering communities. The Council is administered jointly by both the Academies and the Institute of Medicine. Dr. Ralph J. Cicerone and Dr. Charles M. Vest are chair and vice chair, respectively, of the National Research Council.

The **Transportation Research Board** is one of six major divisions of the National Research Council. The mission of the Transportation Research Board is to provide leadership in transportation innovation and progress through research and information exchange, conducted within a setting that is objective, interdisciplinary, and multimodal. The Board's varied activities annually engage about 7,000 engineers, scientists, and other transportation researchers and practitioners from the public and private sectors and academia, all of whom contribute their expertise in the public interest. The program is supported by state transportation departments, federal agencies including the component administrations of the U.S. Department of Transportation, and other organizations and individuals interested in the development of transportation. **www.TRB.org**

www.national-academies.org

CRP STAFF FOR HMCRP REPORT 2

HMCRP PROJECT 06 PANEL

AUTHOR ACKNOWLEDGMENTS

The research reported herein was performed under Dr. Richard G. Lewis, P.E., Principal at HSA Engineers & Scientists. Dr. Ziqi (Zeke) He, P.E., Environmental Engineer with HSA Engineers & Scientists, was responsible for the thermodynamic calculation and design tool. William H. Hutchings, P.G., Professional Geologist with HSA Engineers & Scientists and Ph.D. candidate at the University of South Florida, was responsible for fate transport modeling. Gordon L. Walters, P.E., Environmental Engineer at HSA Engineers & Scientists, was responsible for the tool interface design. Kevin W. Worsham, Database Developer with Conestoga-Rovers & Associates (CRA), and Julie Lidstone, Associate Database Manager with CRA, were responsible for visual basic coding of the tool design. Doug Soutter, Hydrogeologist with CRA, assisted with UNIFAC design. Dr. Hongze Gao, P.E., with CRA, assisted with the screening model design. Ronald Foster, Senior Processing Engineer with CRA, assisted with the data and methodology collection. In addition, the environmental department group at the office of HSA Engineers & Scientists in Fort Myers, Florida, and the emergency response team at CRA's office in Dallas, Texas, participated in data collection of chemical properties and the most commonly transported hazardous materials.

FOREWORD

By William C. Rogers
Staff Officer
Transportation Research Board

HMCRP Report 2: Assessing Soil and Groundwater Impacts of Chemical Mixture Releases from Hazardous Materials Transportation Incidents presents a tool to assess, classify, predict, and quickly communicate fate and transport characteristics of chemical mixtures released into the soil and groundwater as a result of hazardous materials transportation incidents. The tool was developed with a wide range of users in mind. For technical users, the property output table generates the fate and transport properties of an input mixture. For emergency response teams, it provides a quick review of the emergency response requirements of a spill. For non-technical users, a color-coding function is included in the tool to compare the critical fate and transport properties to their pure chemical counterpart and highlight the key parameters affecting the mixture transport in the saturated and unsaturated zones. The tool can also be used to determine whether shipping certain chemicals separately or in mixtures will have significantly higher costs if an incident occurs and to estimate relative costs and timeframes of cleanup after an incident occurs.

Screening models, as well as detailed, computationally intensive models, exist to characterize site-specific impacts on soil and groundwater from hazardous materials releases. These models require various fate and transport parameters as input, which are generally available for pure chemical compounds. However, these parameters are typically unavailable for many of the commonly transported hazardous materials mixtures such as herbicides, paint, cleaning compounds, motor oil, antifreeze, gasoline, and ethanol.

Under HMCRP Project 06, HSA Engineers & Scientists was asked to (1) define and categorize the environmental hazards to soil and groundwater of pure chemicals and mixtures; (2) identify sources and collect readily available data on fate and transport properties; (3) develop a typology and identify and classify common solvents and mixtures that are likely to be transported; (4) develop a typology to estimate the key parameters for different chemical mixtures; (5) design a tool to characterize, predict, and communicate the impact of chemical mixtures in soil and groundwater environments and to estimate the fate and transport parameters of chemical mixtures released to soil and groundwater as a result of hazardous materials transportation incidents; (6) using the tool, estimate the fate and transport parameters for 5 to 10 representative mixtures commonly transported and apply existing basic screening models to estimate impact to soil and groundwater; and (7) refine the tool to compare fate and transport characteristics of pure chemicals to chemical mixtures in order to rank the relative impacts to soil and groundwater.

The chemical mixture tool, a user guide, and the contractor's final report for HMCRP Project 06 can be found on *CRP-CD-90: Chemical Mixture Tool for HMCRP Report 2,* which is bound into this publication. For the convenience of readers, the research team's Tool Design Process Example (Appendix H) and the User Operational Manual (Appendix M) are also provided herein.

CONTENTS

SUMMARY

Assessing Soil and Groundwater Impacts of Chemical Mixture Releases from Hazardous Materials Transportation Incidents

Introduction

Each year, large quantities of hazardous materials are transported throughout the United States. In the event of an incident or accident, these hazardous materials can be released to the environment, thereby impacting soil and groundwater, leading to costly emergency response and cleanup efforts. Many impact measurement techniques in use today concentrate on fatalities/injuries, property damage, and emergency impacts, but exclude environmental and ecological impacts associated with releases into soil, groundwater, aquatic features, or natural habitats. Consequently, risk management decisions are being made in the absence of the comprehensive information necessary to mitigate long-term environmental risk. The screening model developed in this research is meant to aid in addressing this concern. As with all screening model requirements to assess the subsurface impact of hazardous materials, chemical-specific fate and transport data, as well as site-specific data, are necessary input parameters. While the fate and transport data are available for pure chemicals, similar data are not usually available for mixtures of hazardous materials that are commonly transported (e.g., herbicides, paint, cleaning compounds, motor oil, antifreeze, gasoline, and ethanol).

The goal of this research was to develop a tool to estimate the critical fate and transport parameters of chemical mixtures for use in common fate and transport models, allowing the user to efficiently and effectively compare and predict the potential impacts of releases from transportation incidents. Specifically, the developed tool will assess, classify, predict, and quickly communicate fate and transport characteristics of chemical mixtures released into the soil and groundwater as a result of hazardous materials transportation incidents.

The research team has completed 16 months of research on HMCRP Project 06, "Soil and Groundwater Impacts of Chemical Mixture Releases from Hazardous Materials Transportation Incidents." A white paper submitted in June 2009 summarizes the preliminary efforts (Phase I, Tasks 1 to 4 outlined in the contract):

- Task 1—define and categorize the environmental hazards to soil and groundwater of pure chemicals and mixtures,
- Task 2—identify sources and collect readily available data on fate and transport properties,
- Task 3—develop a typology and identify and classify common solvents and mixtures that are likely to be transported by the industry and significantly control or alter the hazardous material fate and transport properties, and
- Task 4—develop a typology to estimate the key parameters for different chemical mixtures.

In September 2009, the research team proceeded to implement Phase 2 (Tasks 5 through 8) of the research project:

- Task 5—design a tool to characterize, predict, and communicate the impact of chemical mixtures in soil and groundwater environments and to estimate the fate and transport parameters of chemical mixtures released to soil and groundwater as a result of hazardous materials transportation incidents;
- Task 6—use the tool to estimate the fate and transport parameters for 5 to 10 representative mixtures commonly transported and to apply existing basic screening models to estimate impact to soil and groundwater;
- Task 7—refine the tool to compare fate and transport characteristics of pure chemicals versus chemical mixtures in order to rank the relative impacts to soil and groundwater; and
- Task 8—prepare a final report that fully explains the tool and documents the entire research effort, explains and justifies recommendations, provides background information used in the development of recommendations that addresses deficiencies and recommends further research.

Consistent with the contract scope, the research team designed the tool using the typology table collected in Phase I as the database and refined the tool using the selected mixtures and existing screening models. The second phase of activity incorporated the data and opinions garnered in Phase I to develop the tool itself. This phase encompassed the design and construction of the tool, and the application of the tool to provide estimates of fate and transport values for several representative mixtures. The tool was then used to determine the effect of changes in these fate-and-transport parameters on the impact to soil and groundwater after a release. *CRP-CD-90: Chemical Mixture Tool for HMCRP Report 2,* provided with this publication, contains the chemical mixture tool, an operational manual for the tool, and the team's final research report for HMCRP Project 06.

Findings

The summary of the literature review and expert interviews is provided for the top-ranked transported or spilled hazardous materials from the Spill Center; Association of American Railroads (AAR); Commodity Flow Survey (CFS); Conestoga-Rovers & Associates emergency response team; and the analysis of the incident reports database search from the Office of Hazardous Materials Safety in the U.S. DOT. Fuels and ethanol-blended fuels, alcohols, acids and bases, paints and related materials are the dominant hazardous material classes according to commodity transported and incidents reported. As identified in the interviews and literature review, the most important mixture is gasoline and ethanol. No clear second mixture was identified, although Not Otherwise Specified (NOS) mixtures clearly make up a large volume of what is transported.

The research team has reviewed and assimilated numerous scientific articles and agency reports regarding chemical fate and transport and the methods for estimating the properties of mixtures, including Raoult's Law, Universal Functional Activity Coefficient (UNIFAC), Cosolvency Effect, and Linear Solvation Energy Relationship (LSER). The approach to estimate the properties of chemical mixtures and the design of a tool have been provided for both ideal and non-ideal chemical mixtures. Considering that UNIFAC has been more versatile over other methods since it works for various solution systems, including those with high nonideality, the research team built a Microsoft Excel UNIFAC (xlUNIFAC) to function as the basis of the chemical mixture tool. This feature is a major strength of UNIFAC and is extremely valuable in estimating solubility of hydrophobic environmental contaminants

in multiple-component systems, which are very difficult to characterize experimentally. In the scenarios where xlUNIFAC does not function for a chemical mixture due to the lack of the molecular volume and surface area (i.e., R_k and Q_k) or the group interaction parameters (i.e., a_{nm}), the cosolvent effects were incorporated into the tool as a second module to estimate the solubilities of chemicals in case of the presence of major cosolvents.

A chemical mixture tool was developed to estimate the fate and transport properties of chemical mixtures using the xUNIFAC model, Raoult's Law, and the Cosolvency—Log K_{ow} Model. The tool is capable of modeling a mixture containing up to 29 components. Approximately 530 chemicals have UNIFAC group assignments, and the linear free energy relationships (LFERs) between the cosolvency power and log K_{ow} are included for 15 completely water-miscible solvents, which are often used in industrial and environmental activities. The output table of the tool consists of the following: (1) chemical identification (name, CAS#, molecular weight), hazardous information (U.S. DOT Hazardous Class and UN/NA#); (2) mixture characteristics (mass percent, volume percent, mole fraction); and (3) physical chemical properties for the input mixture and its components (water solubility, vapor pressure, surface tension, viscosity, partitioning among mixture/water/air, partitioning between water and organic carbon/octanol, diffusion coefficients in air/water/mixture, and half-life time), which can be used to simulate the characteristics of non-aqueous phase liquid (NAPL) (where applicable) in soil, water, and air.

In tests with 11 representative mixtures—including gasoline, methyl tertiary butyl ether (MTBE)-blended gasoline, ethanol-blended gasoline, coal tar, paint, ink, lacquer thinner, and drycleaner solvent—the tool has been versatile at estimating the fate and transport properties of hazardous mixtures. Hydrocarbon Spill Screening Model (HSSM), Multiphase Flow and Multicomponent Transport Model (MOFAT), and BIOSCREEN-AT are used as screening models to simulate the fate and transport of selected mixtures in subsurface. Benzene, toluene, ethylbenzene and xylene (BTEX), particularly benzene, was selected as the target compound to analyze the impact of ethanol and MTBE on gasoline based on the equivalent spill scenarios of oxygenate-free gasoline because benzene is the most mobile gasoline-derived contaminant that possesses significant toxicity and groundwater impact. Results indicated that the presence of 20% ethanol may cause a benzene plume in groundwater to be 30% longer than that in equivalent gasoline under anaerobic conditions, while there were no significant changes in benzene transport under aerobic biodegradation. The MTBE addition to gasoline does not significantly affect the gasoline component transport. However, the effect of MTBE itself on the environment is a concern due to MTBE's high water solubility and low biodegradation under both aerobic and anaerobic conditions.

Conclusions

The chemical mixture tool was developed with a wide range of users in mind. For highly technical users, the property output table generates the fate and transport properties of an input mixture. For emergency response teams, the emergency response guide provides a quick review of the emergency response to a spill. For non-technical users, a color-coding function is included in the tool to compare the critical fate and transport properties to their pure chemical counterparts and highlight the key parameters affecting the mixture transport in the unsaturated (i.e., vadose) zone. A simplified version of Domenico's model, designed by the research team, is included to simulate chemical fate and transport in groundwater. Without the availability of external screening models, the research team screening model can be applied directly to simulate the transport of a hazardous mixture in groundwater.

Tool comparison, calibration, sensitivity analysis, and uncertainty analysis showed that the tool estimates mixture properties (e.g., interfacial tension and viscosity) within a mean

error of 30% and the NAPL-water interface properties (e.g., solubility and partition coefficient) within a maximum factor of 5.0, which is relatively small compared with the imprecise knowledge of subsurface gasoline release volumes and scenarios. When data are not available, this tool can be utilized to estimate the properties of a mixture.

The tool results can be used to determine whether shipping certain chemicals separately or in mixtures will have significantly higher costs if an incident occurs, aiding in the emergency planning costs. The tool results can be used to estimate the relative costs and timeframes of cleanup after an incident occurs. The tool can also be used by remediation engineers to provide better remediation alternatives, given the availability of different properties of mixtures versus pure chemicals. For example, regulators and scientists could use the tool to estimate the properties of novel additives in future fuel formulations and thereby provide key inputs for determining the transportation facility upgrade and assessing environmental transport of these compounds using external screening models.

Tool Limitations and Future Research Recommendations

The main limitation of the tool is that it cannot be used for all chemical substances contained in the database of approximately 740 components derived from literary research and interviews with professional personnel based on hazardous material classification and commodity flow survey and incident reports. That said, data for new chemicals can be added as pure-phase information becomes available. The intended application domain is for liquid organic chemicals, particularly petroleum and related compounds. Inorganic and organometallic chemicals generally are outside the tool's domain. Future work may be focused on the expansion of the typology table database to a larger database to simulate mixtures that consist of more chemicals. In addition, further research is needed to update the xlUNIFAC parameters with the latest available data. For example, as the largest database, the commercial UNIFAC still lacks parameters for some halogenated compounds and new pharmaceutical compounds.

This study is focused on the mixture source zone property estimate. Therefore, the chemical property parameters were calculated based on the assumption that the NAPL and groundwater reach equilibria for individual components. The kinetic process of the interaction zone was not considered, and the interaction between the NAPL source zone and the dissolved plume in groundwater was not modeled in this study. For example, half-life time was produced by the tool for anaerobic and aerobic conditions from the typology table, which does not represent site-specific decay. Although the tool generates property parameters with a factor of 5.0, field assessment is necessary to further calibrate the tool for modification to simulate the field spill scenarios. The tool will not be able to assess the property changes with the temporal NAPL composition changes or the decay in the downgradient groundwater. For example, the rapid transfer of ethanol from gasoline into the water in the vadose zone (e.g., small volume spills) may not change the gasoline bulk transport properties (e.g., interfacial tension and viscosity) as predicted in this study. Furthermore, the quick degradation of ethanol in the groundwater will alter the cosolvency power, as well as the biodegradation of other components. Improved tool modification is required to integrate the mixture degradation in the field, especially the ethanol effect on the biodegradation of BTEX in the downgradient of the plumes.

A screening model has been incorporated within the tool for the users to simulate the fate and transport in groundwater. However, the screening model results by HSSM and MOFAT indicate that the mixtures have dramatically different transport in the unsaturated zone due to changes in the density, interfacial tension, and viscosity. The behavior of the mixture in the unsaturated zone will significantly affect the groundwater fate and transport. Therefore,

combined with the existing groundwater model, further research is necessary to design a vadose zone screening model to simulate the mixture fate in subsurface based on the spill scenarios (e.g., spill volume, mixture component, and site-specific hydrogeologic setting). A user-friendly unit conversion may be included within the tool to export the tool results directly to the required form of screening models.

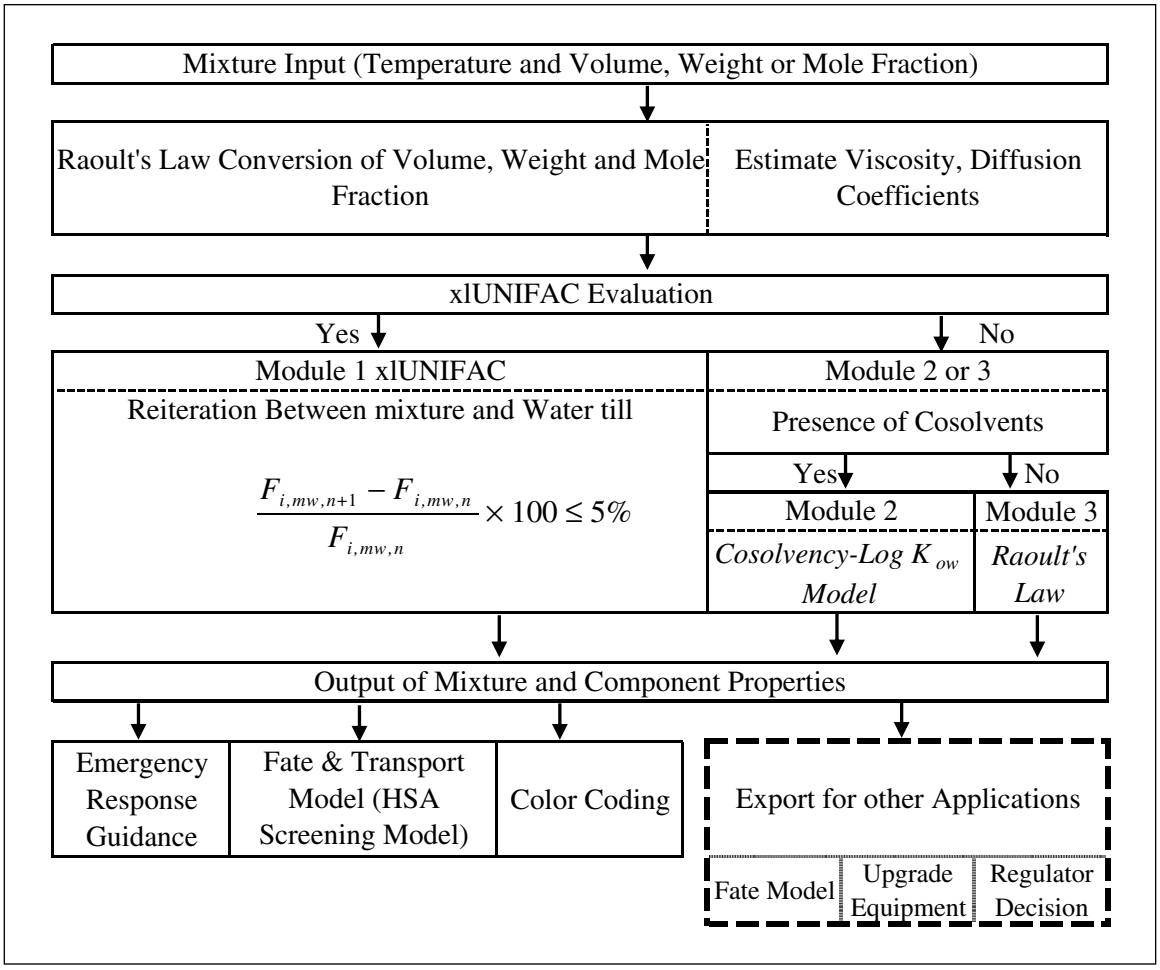
Although the color-coding function is designed in the tool to compare the fate and transport characteristics of pure chemicals versus chemical mixtures in order to rank the relative impacts to soil and groundwater, future research is needed to compare the concentrations in subsurface to EPA clean up levels and to consider the cost and time frame of active remediation compared to natural attenuation. This module may be designed to estimate the cost of the most commonly used remedial approaches (e.g., groundwater pump-treat, air sparging, soil vapor extraction, chemical oxidation, and enhanced natural attenuation) at different time frames after the incident spills.

The current version of the chemical mixture tool, provided on *CRP-CD-90,* was designed and tested to work with the PC version of Microsoft Excel. Additional research may be needed to modify the tool to work with a Mac system.

Contents of Contractor's Final Report for HMCRP Project 06
(Final Report Contained on *CRP-CD-90*)

APPENDIX H

Tool Design Process Example



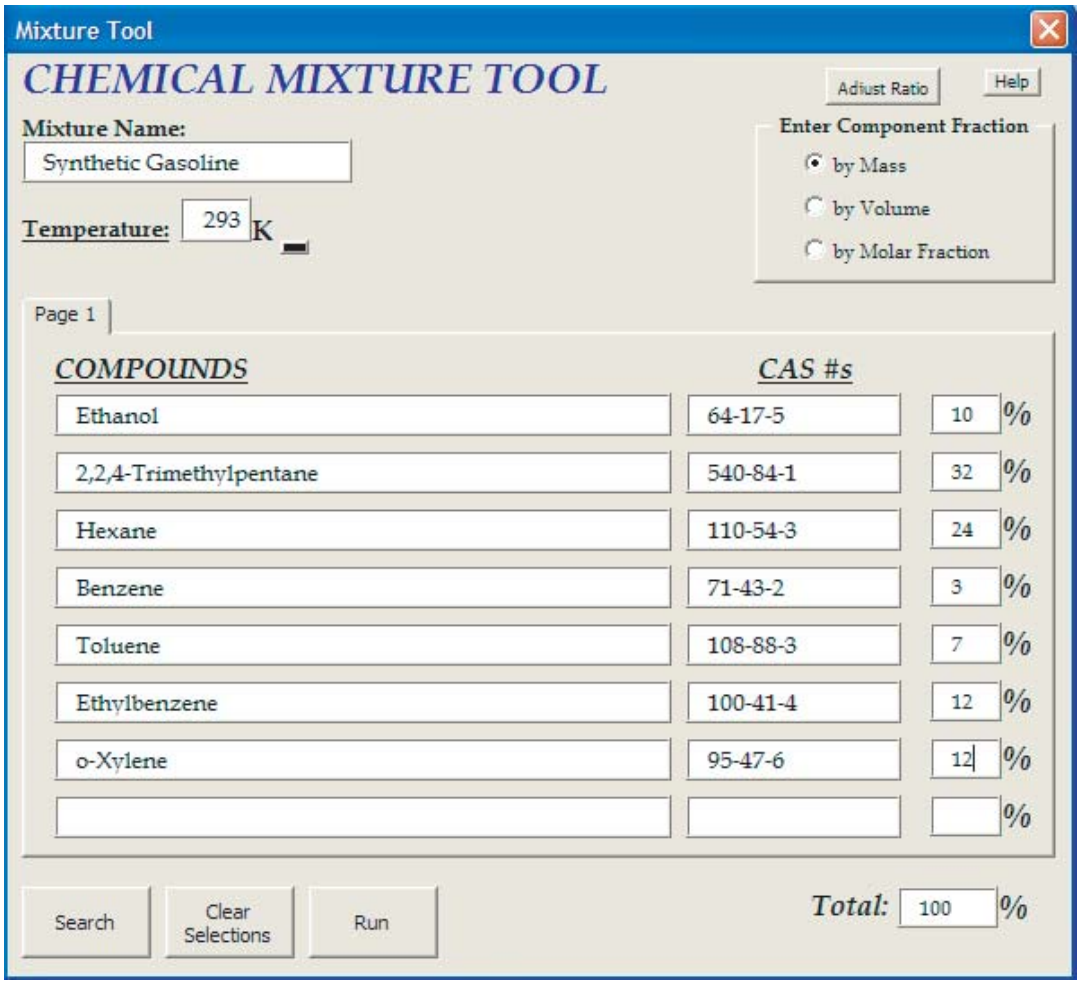
Final Tool Design Flow Chart for Mixture Properties

Two examples are provided to elucidate the tool design process for the fate and transport properties of an input mixture as well as its components. One is for the Module 1 through a synthetic gasoline as a mixture example and the other is for Module 2 and 3 through a mixture of alcohols and chlorinated solvents. These design processes are hidden in the final tool and not formatted. In addition, emergency response guidance, HSA screening model, and the color-coding processes are not discussed in these two examples (details refer to the descriptions in the report for each section).

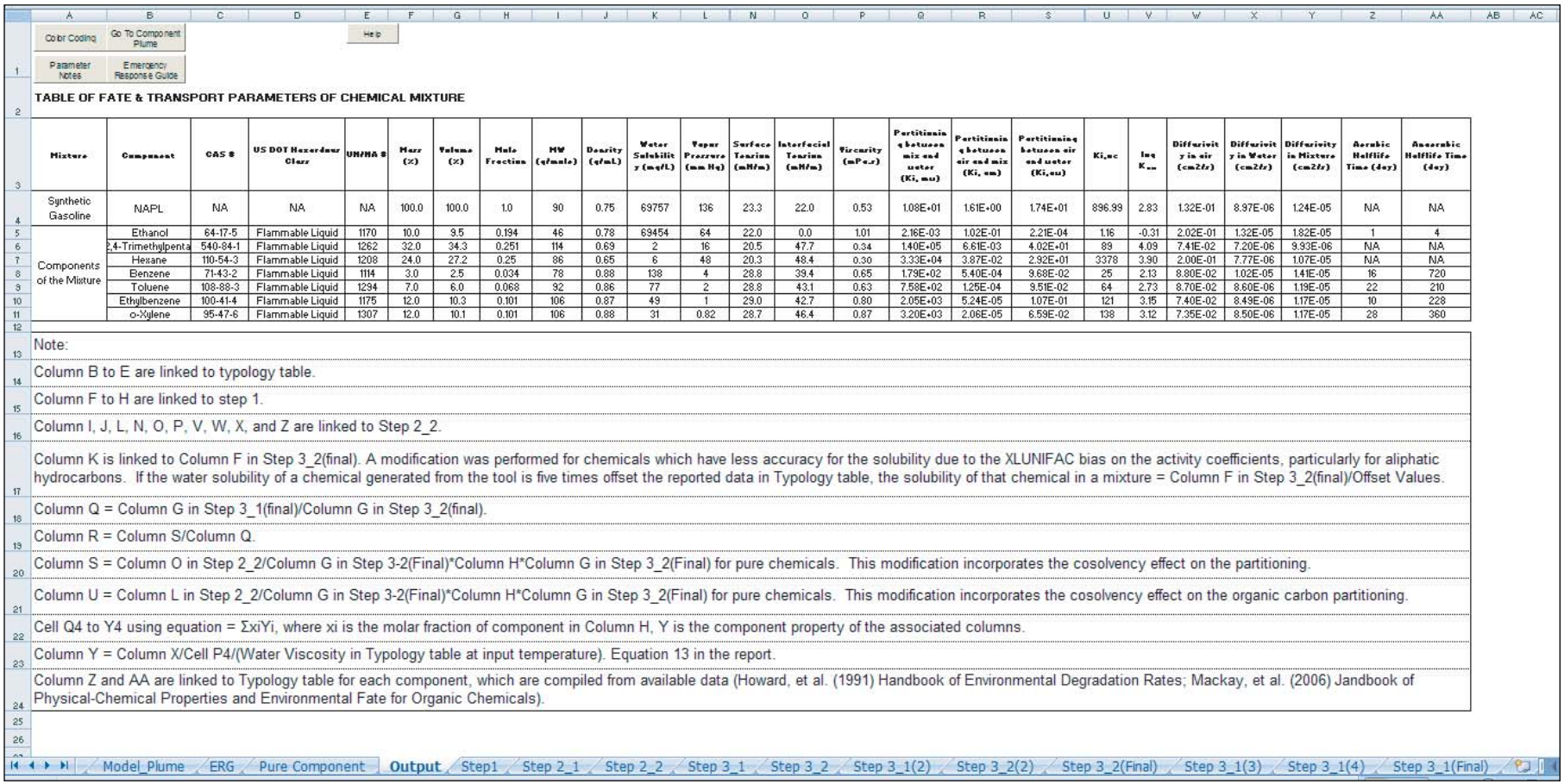
The tool is designed to run the input mixture as a pseudo component NAPL. In order to compare the component properties in a mixture to its pure phase, the tool will also run each individual component as a 100% input. Shown below are the output table of the mixture and the pure components. Clearly, there are many calculation worksheets to obtain these final output tables. The number of the calculation step depends on the input mixture properties. Each step is provided below with notes of the calculation process beneath the tables (Equations are provided in the report).

Example 1. Synthetic Gasoline

The mixture components and the mass fractions are shown in the Input Interface below.



Mixture Input Interface of Example 1.



Color Coding | Go To Component Plume | Help | Parameter Notes | Emergency Response Guide

TABLE OF FATE & TRANSPORT PARAMETERS OF CHEMICAL MIXTURE

Mixture	Component	CAS #	US DOT Hazardous Class	UN/NA #	Mass (%)	Volume (%)	Mole Fraction	MW (g/mole)	Density (g/mL)	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Partitioning between mix and water (Ki, mw)	Partitioning between air and mix (Ki, am)	Partitioning between air and water (Ki,aw)	Ki,ac	log Koc	Diffusivity in air (cm2/s)	Diffusivity in Water (cm2/s)	Diffusivity in Mixture (cm2/s)	Aerobic Halflife Time (day)	Anaerobic Halflife Time (day)
Synthetic Gasoline	NAPL	NA	NA	NA	100.0	100.0	1.0	90	0.75	69757	136	23.3	22.0	0.53	1.08E+01	1.61E+00	1.74E+01	896.99	2.83	1.32E-01	8.97E-06	1.24E-05	NA	NA
Components of the Mixture	Ethanol	64-17-5	Flammable Liquid	1170	10.0	9.5	0.194	46	0.78	69454	64	22.0	0.0	1.01	2.16E-03	1.02E-01	2.21E-04	1.16	-0.31	2.02E-01	1.32E-05	1.82E-05	1	4
	2,4-Trimethylpenta	540-84-1	Flammable Liquid	1262	32.0	34.3	0.251	114	0.69	2	16	20.5	47.7	0.34	1.40E+05	6.61E-03	4.02E+01	89	4.09	7.41E-02	7.20E-06	9.93E-06	NA	NA
	Hexane	110-54-3	Flammable Liquid	1208	24.0	27.2	0.25	86	0.65	6	48	20.3	48.4	0.30	3.33E+04	3.87E-02	2.92E+01	3378	3.90	2.00E-01	7.77E-06	1.07E-05	NA	NA
	Benzene	71-43-2	Flammable Liquid	1114	3.0	2.5	0.034	78	0.88	138	4	28.8	39.4	0.65	1.79E+02	5.40E-04	9.68E-02	25	2.13	8.80E-02	1.02E-05	1.41E-05	16	720
	Toluene	108-88-3	Flammable Liquid	1294	7.0	6.0	0.068	92	0.86	77	2	28.8	43.1	0.63	7.58E+02	1.25E-04	9.51E-02	64	2.73	8.70E-02	8.60E-06	1.19E-05	22	210
	Ethylbenzene	100-41-4	Flammable Liquid	1175	12.0	10.3	0.101	106	0.87	49	1	29.0	42.7	0.80	2.05E+03	5.24E-05	1.07E-01	121	3.15	7.40E-02	8.49E-06	1.17E-05	10	228
	o-Xylene	95-47-6	Flammable Liquid	1307	12.0	10.1	0.101	106	0.88	31	0.82	28.7	46.4	0.87	3.20E+03	2.08E-05	6.59E-02	138	3.12	7.35E-02	8.50E-06	1.17E-05	28	360

Note:

Column B to E are linked to typology table.

Column F to H are linked to step 1.

Column I, J, L, N, O, P, V, W, X, and Z are linked to Step 2_2.

Column K is linked to Column F in Step 3_2(final). A modification was performed for chemicals which have less accuracy for the solubility due to the XLUNIFAC bias on the activity coefficients, particularly for aliphatic hydrocarbons. If the water solubility of a chemical generated from the tool is five times offset the reported data in Typology table, the solubility of that chemical in a mixture = Column F in Step 3_2(final)/Offset Values.

Column Q = Column G in Step 3_1(final)/Column G in Step 3_2(final).

Column R = Column S/Column Q.

Column S = Column O in Step 2_2/Column G in Step 3-2(Final)*Column H*Column G in Step 3_2(Final) for pure chemicals. This modification incorporates the cosolvency effect on the partitioning.

Column U = Column L in Step 2_2/Column G in Step 3-2(Final)*Column H*Column G in Step 3_2(Final) for pure chemicals. This modification incorporates the cosolvency effect on the organic carbon partitioning.

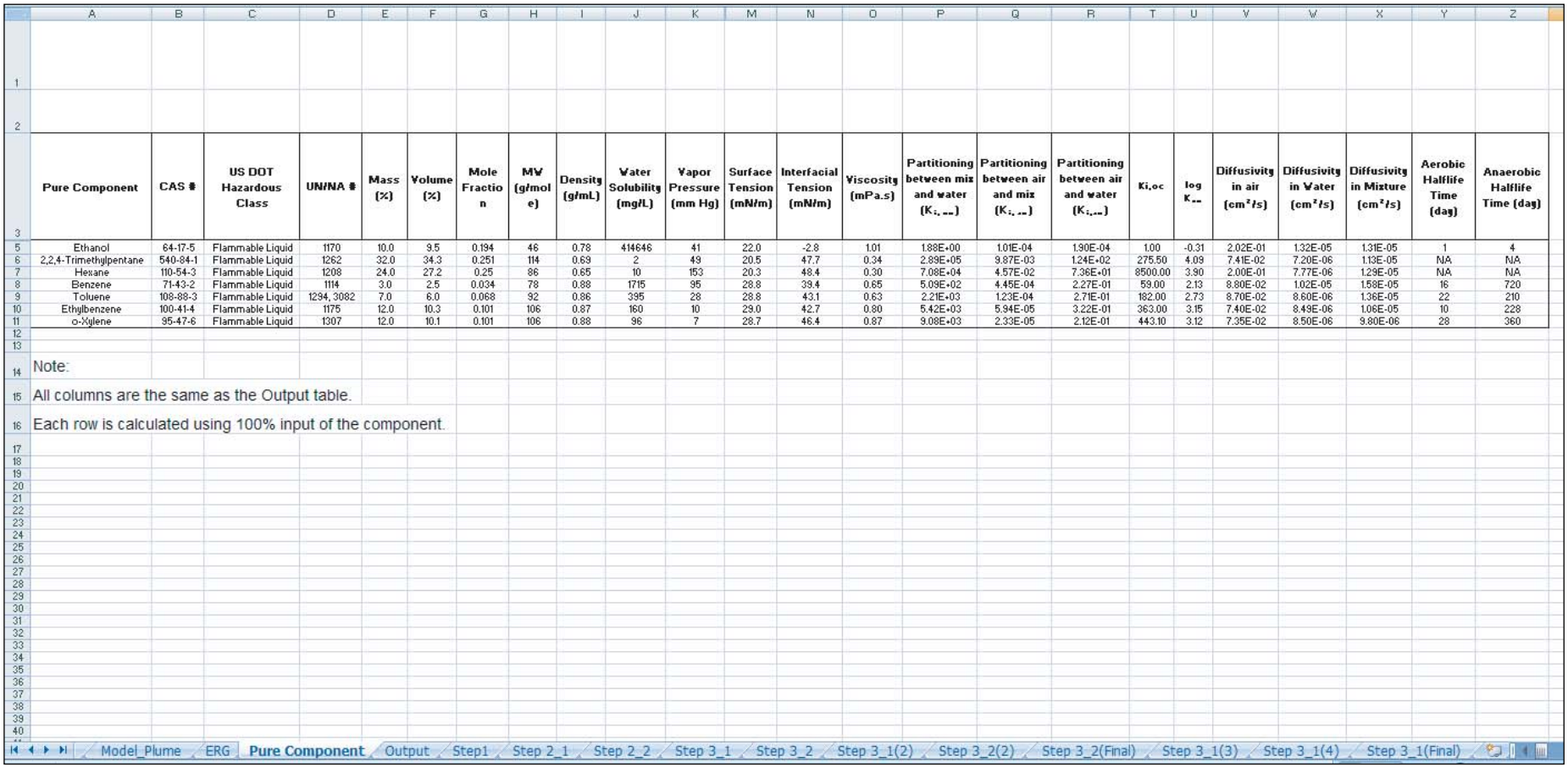
Cell Q4 to Y4 using equation = ΣxiYi, where xi is the molar fraction of component in Column H, Y is the component property of the associated columns.

Column Y = Column X/Cell P4/(Water Viscosity in Typology table at input temperature). Equation 13 in the report.

Column Z and AA are linked to Typology table for each component, which are compiled from available data (Howard, et al. (1991) Handbook of Environmental Degradation Rates; Mackay, et al. (2006) Jandbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals).

Model_Plume | ERG | Pure Component | Output | Step1 | Step 2_1 | Step 2_2 | Step 3_1 | Step 3_2 | Step 3_1(2) | Step 3_2(2) | Step 3_2(Final) | Step 3_1(3) | Step 3_1(4) | Step 3_1(Final)

Output Table of Example 1.



Pure Component	CAS #	US DOT Hazardous Class	UN/NA #	Mass (%)	Volume (%)	Mole Fraction	MW (g/mole)	Density (g/mL)	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Partitioning between mix and water ($K_{i,m}$)	Partitioning between air and mix ($K_{i,m}$)	Partitioning between air and water ($K_{i,w}$)	$K_{i,oc}$	log K_{ow}	Diffusivity in air (cm^2/s)	Diffusivity in Water (cm^2/s)	Diffusivity in Mixture (cm^2/s)	Aerobic Halflife Time (day)	Anaerobic Halflife Time (day)
Ethanol	64-17-5	Flammable Liquid	1170	10.0	9.5	0.194	46	0.78	414646	41	22.0	-2.8	1.01	1.88E+00	1.01E-04	1.90E-04	1.00	-0.31	2.02E-01	1.32E-05	1.31E-05	1	4
2,2,4-Trimethylpentane	540-84-1	Flammable Liquid	1262	32.0	34.3	0.251	114	0.69	2	49	20.5	47.7	0.34	2.89E+05	9.87E-03	1.24E+02	275.50	4.09	7.41E-02	7.20E-06	1.13E-05	NA	NA
Hexane	110-54-3	Flammable Liquid	1208	24.0	27.2	0.25	86	0.65	10	153	20.3	48.4	0.30	7.08E+04	4.57E-02	7.36E+01	8500.00	3.90	2.00E-01	7.77E-06	1.29E-05	NA	NA
Benzene	71-43-2	Flammable Liquid	1114	3.0	2.5	0.034	78	0.88	1715	95	28.8	39.4	0.65	5.09E+02	4.45E-04	2.27E-01	59.00	2.13	8.80E-02	1.02E-05	1.58E-05	16	720
Toluene	108-88-3	Flammable Liquid	1294, 3082	7.0	6.0	0.068	92	0.86	395	28	28.8	43.1	0.63	2.21E+03	1.23E-04	2.71E-01	182.00	2.73	8.70E-02	8.60E-06	1.36E-05	22	210
Ethylbenzene	100-41-4	Flammable Liquid	1175	12.0	10.3	0.101	106	0.87	160	10	29.0	42.7	0.80	5.42E+03	5.94E-05	3.22E-01	363.00	3.15	7.40E-02	8.49E-06	1.06E-05	10	228
o-Xylene	95-47-6	Flammable Liquid	1307	12.0	10.1	0.101	106	0.88	96	7	28.7	46.4	0.87	9.08E+03	2.33E-05	2.12E-01	443.10	3.12	7.35E-02	8.50E-06	9.80E-06	28	360

Note:

All columns are the same as the Output table.

Each row is calculated using 100% input of the component.

Model_Plume | ERG | Pure Component | Output | Step1 | Step 2_1 | Step 2_2 | Step 3_1 | Step 3_2 | Step 3_1(2) | Step 3_2(2) | Step 3_2(Final) | Step 3_1(3) | Step 3_1(4) | Step 3_1(Final)

Pure Component Output Table of Example 1.

	A	B	C	D	E	F	G
1	**Step 1. Inputs and conversions**						
2	Synthetic gasoline	CAS#	Conversion of component fraction				
3			mass%	mass/density	vol %	mass/MW	Molar fraction
4	Ethanol	64-17-5	10	12.821	9.517	0.217	0.194
5	2,2,4-Trimethylpentane	540-84-1	32	46.247	34.329	0.28	0.251
6	Hexane	110-54-3	24	36.652	27.207	0.278	0.25
7	Benzene	71-43-2	3	3.414	2.534	0.038	0.034
8	Toluene	108-88-3	7	8.106	6.017	0.076	0.068
9	Ethylbenzene	100-41-4	12	13.841	10.274	0.113	0.101
10	o-Xylene	95-47-6	12	13.635	10.121	0.113	0.101
11	Total		100	134.715	100	1.116	1.0
12	Temperature	°C	20				
13		K	293				
14		°F	68				
15							
16	Note:						
17	Column C: Red color highligthed are the input data of the mixture.						
18	Temperature is an input parameter too, which will be used in viscosity and diffusion coefficient calculation.						
19	Column D = Column C/density in typology table.						
20	Column E = Column D/Cell D7*100.						
21	Column F = Column C/molecular weight in typology table.						
22	Column G = Column F/Cell F7*100.						
23							

Tool Step 1 of Example 1.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	**Step 2_1. Mixture Phase Properties**													
2	Compound	CAS #	Mole fraction in NAPL	Molar Concentration (mole/L)	MW (g/mole)	Density (g/ml)	Molar Volume (ml)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Activity Coefficient in mix	Individual Vapor Pressure (mm Hg)	Total Vapor Pressure (mm Hg)	
3	Ethanol	64-17-5	0.194	1.638							3.95E+00	6.36E+01		
4	2,2,4-Trimethylpentane	540-84-1	0.251	2.114							1.29E+00	1.59E+01		
5	Hexane	110-54-3	0.25	2.102							1.26E+00	4.79E+01		
6	Benzene	71-43-2	0.034	0.29	89.59	0.75	118.72	23.28	22.00	0.53	1.24E+00	4.05E+00	136.00	
7	Toluene	108-88-3	0.068	0.573							1.27E+00	2.46E+00		
8	Ethylbenzene	100-41-4	0.101	0.853							1.26E+00	1.23E+00		
9	o-Xylene	95-47-6	0.101	0.853							1.22E+00	8.16E-01		
10	Total		1.00	8.423										
11														
12	Note:													
13	Column C = Column G in Step 1.													
14	Column D = Column C/Column G*1000.													
15	Column E to H using equation = $\Sigma xiYi$, where xi is the molar fraction of component I, Y is the component property of MW, density, molar volume, and surface tension (Equation 8-10 in the report).													
16	Column I using equation = $\sigma_{i,W} = -10/3\text{-}7.21*\ln(X_O + X_W)$ (dynes/cm), where Xo - mole faction of organic phase in water, Xw - mole faction of water in organic phase, which are the final results of the reiterateing calculation (step 3_2(3) and Step 3_1(5) in this example). Equation 11 in the report.													
17	Column J using equation = $(\Sigma xi(Yi)^{1/n})^n$, where xi is the molar fraction of component I, n is the total component number, Yi is the component viscosity calculated using different equations for each group chemcicals (Equation 12 and 12a in the report).													
18	Columnu K is the activity coefficiency of component I in the mixture calculated using XLUNIFAC with the input of component molar fraction and the group info in typology table (Column U to AJ), using input temperate 293 K. Equation 20 to 20b4 in the report.													
19	Column L will be $\gamma i*xi*VPi$, γi is the activity coef in column K, Vpi is the puer compound vapor pressure in typolgy Table Column K. Equation 1 in the report.													
20	Column M is the sum of Column K. Equation 6 in the report.													

Tool Step 2_1 of Example 1.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	Step 2_2. Aqueous Phase Properties														
2	Compound	CAS #	Mole fraction in NAPL	Solubility (mg/L)	Solubility (mole/L)	Solubility (mole fraction)	Activity Coefficient in water	Diffusity in Air (cm^2/s)	Diffusity in Water (cm^2/s)	Aerobic Half-life time (days)	Anaerobic Half-life time (days)	Partitioning between organic carbon and water (Ki,oc)	Henry's Law Constant ($atm\text{-}m^3/mole$)	Partitioning between mix and water (Ki,mw)	Partitioning between air and water (Ki,aw)
3	Ethanol	64-17-5	0.194	7.68E+05	1.65E+01	2.29E-01	1.94E+00	2.02E-01	1.32E-05	1.10E+00	4.30E+00	1.00E+00	4.66E-06	9.83E-02	1.90E-04
4	2,2,4-Trimethylpentane	540-84-1	0.251	7.88E-01	3.83E-04	3.11E-01	8.65E+02	7.41E-02	7.20E-06	1.10E+04	1.10E+04	2.76E+02	3.04E+00	3.07E+05	1.24E+02
5	Hexane	110-54-3	0.25	2.98E+00	3.06E-03	3.09E-01	2.49E+02	2.00E-01	7.77E-06	1.10E+04	1.10E+04	8.50E+03	1.80E+00	6.08E+04	7.36E+01
6	Benzene	71-43-2	0.034	7.64E+01	1.77E-03	4.24E-02	1.11E+02	8.80E-02	1.02E-05	1.60E+01	7.20E+02	5.90E+01	5.55E-03	2.96E+02	2.27E-01
7	Toluene	108-88-3	0.068	4.56E+01	8.32E-04	8.43E-02	2.55E+02	8.70E-02	8.60E-06	2.20E+01	2.10E+02	1.82E+02	6.64E-03	1.16E+03	2.71E-01
8	Ethylbenzene	100-41-4	0.101	2.16E+01	4.59E-04	1.26E-01	4.65E+02	7.40E-02	8.49E-06	1.00E+01	2.28E+02	3.63E+02	7.88E-03	4.20E+03	3.22E-01
9	o-Xylene	95-47-6	0.101	2.20E+01	2.94E-04	1.26E-01	5.42E+02	7.35E-02	8.50E-06	2.80E+01	3.60E+02	4.43E+02	5.18E-03	4.12E+03	2.12E-01
10	Water														
11															
12	Note:														
13	Column C = Column G in Step 1.														
14	Column D: solubility = γi*xi*Si = ColumnC*"Setp2_1"column K*"typology"Column M. Euqation 2 in the report.														
15	Column E = Column D/"typology" Column G.														
16	Column F = Column E/(55.6+the sum of Column E). Here assume 1:1 NAPL to Water volume ratio. With the adjust of the ratio, the calculation will be different.														
17	Column G is the results of XLUNIFAC from Column F.														
18	Column H to M are the columns in typology table. Column H and I in the Typology table were calcualted using Equation 13a, 13 b, 13 b1 in the report.														
19	Column N = Column D in Step 2_1/Column E.														
20	Column O = Column M*40.8745 to convert Hendy's Law Constant to unitless.														
21															

Tool Step 2_2 of Example 1.

	A	B	C	D
1	**Step 3_1. Equilibrium in Mixture NAPL Phase**			
2	Component	Moles	Mole fraction	Act. Coefficient
3	Ethanol	1.64E+00	1.94E-01	3.92E+00
4	2,2,4-Trimethylpentane	2.11E+00	2.51E-01	1.29E+00
5	Hexane	2.10E+00	2.49E-01	1.26E+00
6	Benzene	2.90E-01	3.44E-02	1.24E+00
7	Toluene	5.73E-01	6.80E-02	1.28E+00
8	Ethylbenzene	8.53E-01	1.01E-01	1.26E+00
9	o-Xylene	8.53E-01	1.01E-01	1.22E+00
10	Water	1.00E-02	1.19E-03	6.38E+01
11				
12	Note:			
13	Column B is from Column E in Step 2_2.			
14	Column C is the mole fraction based on Column B.			
15	Column D if the XLUNIFAC results from Column C.			
16				

Tool Step 3_1 of Example 1.

	A	B	C	D
1	**Step 3_2. Equilibrium in Aqueous Phase**			
2	Component	Moles	Mole fraction	Act. Coefficient
3	Ethanol	1.491586E+00	2.61E-02	5.94E+00
4	2,2,4-Trimethylpentane	6.897513E-06	1.21E-07	4.85E+04
5	Hexane	3.454527E-05	6.05E-07	5.92E+03
6	Benzene	9.753252E-04	1.71E-05	1.50E+03
7	Toluene	4.945796E-04	8.66E-06	6.62E+03
8	Ethylbenzene	2.031310E-04	3.56E-06	1.74E+04
9	o-Xylene	2.068049E-04	2.72E+04	
10	Water	5.559000E+01	1.00E+00	
11				
12	Note:			
13	Column B = Column B in Step 3_1/(1+Column N in Step 2_2). Here assume 1:1 NAPL to Water volume ratio. With the adjust of the ratio, the calculation will be different. So water mole is 55.6 - Cell B10 in Step 3_1.			
14	Column C is the mole fraction based on Column B.			
15	Column D if the XLUNIFAC results from Column C.			

Tool Step 3_2 of Example 1.

	A	B	C	D	E
1	**Step 3_1 (2). Equilibrium in Mixture NAPL Phase**				
2	Component	Moles	Mole fraction	Act. Coefficient	<10% stop
3	Ethanol	1.47E-01	2.08E-02	1.03E+01	-89.28%
4	2,2,4-Trimethylpenta	2.11E+00	3.00E-01	1.08E+00	19.83%
5	Hexane	2.10E+00	2.99E-01	1.08E+00	19.83%
6	Benzene	2.89E-01	4.10E-02	1.17E+00	19.43%
7	Toluene	5.73E-01	8.14E-02	1.21E+00	19.73%
8	Ethylbenzene	8.53E-01	1.21E-01	1.16E+00	19.80%
9	o-Xylene	8.53E-01	1.21E-01	1.16E+00	19.80%
10	Water	1.08E-01	1.53E-02	3.33E+02	1190.93%
11					
12	Note:				
13	Column B = Column B in Step 3_1/(1+Column N in Step 2_2). Here assume				
14	Column C is the mole fraction based on Column B.				
15	Column D if the XLUNIFAC results from Column C.				
16	Column E = (Cloumn C - Column C in step 3_1)/Column C in Step 3_1.				
17					

Tool Step 3_1(2) of Example 1.

	A	B	C	D
1	**Step 3_2 (2). Equilibrium in Aqueous Phase**			
2	Component	Mole fraction	Act. Coefficient	<10% stop
3	Ethanol	2.86E-02	5.80E+00	9.53%
4	2,2,4-Trimethylpentane	6.71E-06	4.48E+04	5452.57%
5	Hexane	5.45E-05	5.56E+03	8910.24%
6	Benzene	3.19E-05	1.43E+03	86.98%
7	Toluene	1.48E-05	6.21E+03	71.11%
8	Ethylbenzene	8.11E-06	1.62E+04	127.87%
9	o-Xylene	5.16E-06	2.52E+04	42.55%
10	Water	9.71E-01	1.00E+00	-0.26%
11				
12	Note:			
13	Column B = Column C in Step 3_1(2)*Column D in Step 3_1(2)/Column D in Step 3_2.			
14	Column C if the XLUNIFAC results from Column B.			
15	Column D = (Cloumn B - Column C in step 3_2)/Column C in Step 3_2.			
16				

Tool Step 3_2(2) of Example 1.

	A	B	C	D	E	F	G	H	I	J	K
1	**Step 3_2 (Final). Equilibrium in Aqueous Phase**										
2	Component	Act. Coefficient	Mole fraction	<10% stop	mass (moles)	Solubility (mg/L)	Solubility (mole/L)	MW (g/mole)	Density (g/mL)	Molar Volume (mL)	
3	Ethanol	5.80E+00	2.86E-02	0.00%	1.64E+00	6.95E+04	1.51E+00				
4	2,2,4-Trimethylpentane	4.47E+04	7.27E-06	8.36%	4.15E-04	4.37E+01	3.83E-04				
5	Hexane	5.56E+03	5.81E-05	6.48%	3.32E-03	2.64E+02	3.06E-03				
6	Benzene	1.43E+03	3.36E-05	5.19%	1.92E-03	1.38E+02	1.77E-03	18.83	0.99	18.98	
7	Toluene	6.21E+03	1.58E-05	6.60%	9.03E-04	7.67E+01	8.32E-04				
8	Ethylbenzene	1.62E+04	8.71E-06	7.37%	4.97E-04	4.87E+01	4.59E-04				
9	o-Xylene	2.51E+04	5.58E-06	8.02%	3.19E-04	3.12E+01	2.94E-04				
10	Water	1.00E+00	9.71E-01	0.00%	5.55E+01	9.22E+05	5.12E+01				
11											
12	Note:										
13	Column B and C: Reiterating Step 3-2(2) and stop when Column D is < 10%.										
14	Column D = (Cloumn C - Column C in step 3_2(previous))/Column C in Step 3_2(previous).										
15	Column E calculated based on Column C. Cell E10 = 55.6 - Column B10 in Step 3-1(2). Here assume 1:1 NAPL to Water volume ratio. With the adjust of the ratio, the calculation will be different. So water mole is 55.6 - Cell B10 in Step 3_1.										
16	Column F = Column G * MW in Typology table.										
17	Column G = Column C/Column J * 1000.										
18	Column H and I using equation = ΣxiYi, where xi is the molar fraction of component in Column C, Y is the component property of MW and density.										
19	Column J = Column H/Column I.										
20											

Tool Step 3_2(Final) of Example 1.

	A	B	C	D	E
1	**Step 3_1 (3). Equilibrium in Mixture NAPL Phase**				
2	Component	Moles	Mole fraction	Act. Coefficient	<10% stop
3	Ethanol	2.96E-03	4.35E-04	1.62E+01	-97.91%
4	2,2,4-Trimethylpentane	2.11E+00	3.11E-01	1.06E+00	3.46%
5	Hexane	2.10E+00	3.09E-01	1.06E+00	3.32%
6	Benzene	2.88E-01	4.23E-02	1.18E+00	3.15%
7	Toluene	5.72E-01	8.42E-02	1.21E+00	3.41%
8	Ethylbenzene	8.53E-01	1.25E-01	1.17E+00	3.45%
9	o-Xylene	8.53E-01	1.25E-01	1.16E+00	3.47%
10	Water	1.99E-02	2.93E-03	8.47E+02	-80.87%
11					
12	Note:				
13	Column B = Column B in Step 3_1- Column B in Step 3_2)(final). Set as previous value if negative.				
14	Cell B10 = SUM(B4:B9)*'Step 3-2 (4)'!B10*'Step 3-2 (4)'!C10/'Step 3-1 (3)'!D10/(1-'Step 3-2 (4)'!C10*'Step 3-2 (4)'!B10/'Step 3-1 (3)'!D10)				
15	Column C is the mole fraction based on Column B.				
16	Column D if the XLUNIFAC results from Column C.				
17	Column E = (Cloumn C - Column C in step 3_1)/Column C in Step 3_1.				
18					
19					

Tool Step 3_1(3) of Example 1.

	A	B	C	D	E
1	**Step 3_1 (4). Equilibrium in Mixture NAPL Phase**				
2	Component	Moles	Mole fraction	Act. Coefficient	<10% stop
3	Ethanol	2.96E-03	4.36E-04	1.69E+01	0.18%
4	2,2,4-Trimethylpentane	2.11E+00	3.11E-01	1.06E+00	0.18%
5	Hexane	2.10E+00	3.09E-01	1.06E+00	0.18%
6	Benzene	2.88E-01	4.24E-02	1.18E+00	0.18%
7	Toluene	5.72E-01	8.43E-02	1.21E+00	0.18%
8	Ethylbenzene	8.53E-01	1.26E-01	1.17E+00	0.18%
9	o-Xylene	8.53E-01	1.26E-01	1.16E+00	0.18%
10	Water	7.81E-03	1.15E-03	9.36E+02	-60.70%
11					
12	Note:				
13	Repeat Step 3_1(3).				
14					

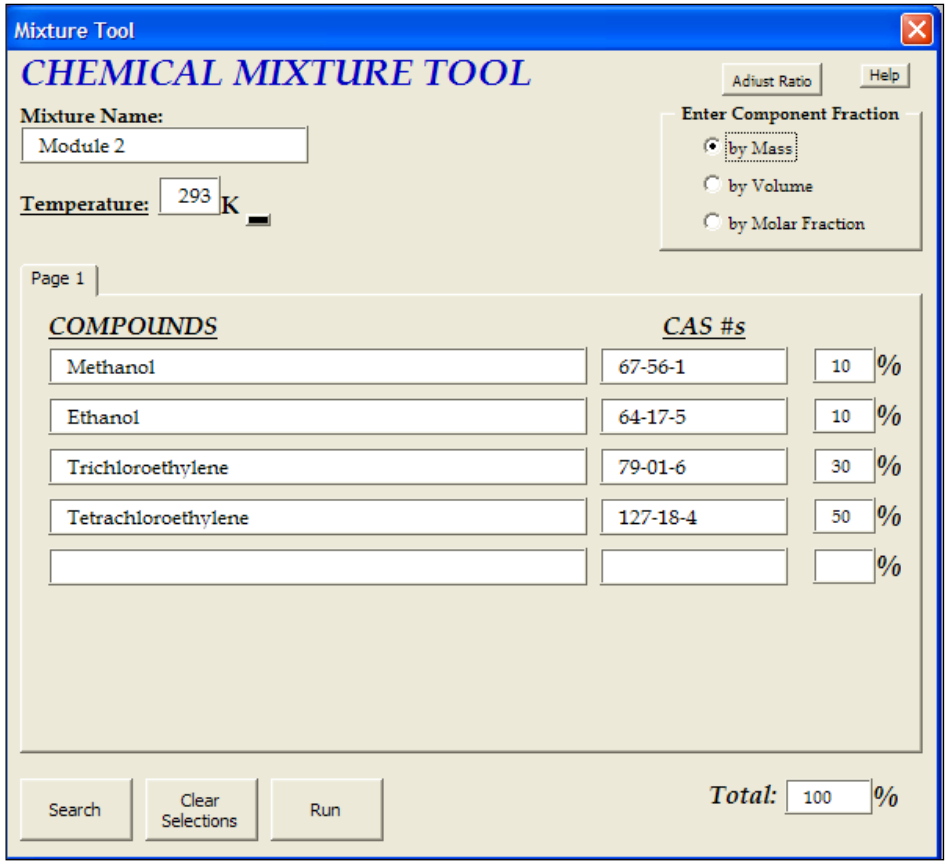
Tool Step 3_1(4) of Example 1.

	A	B	C	D	E	F	G	H	I	J	K
1	**Step 3_1 (Final). Equilibrium in Mixture NAPL Phase**										
2	Component	Act. Coefficient	Mole fraction	Moles	<10% stop	Solubility (mg/L)	Solubility (mole/L)	MW (g/mole)	Density (g/mL)	Molar Volume (mL)	
3	Ethanol	1.69E+01	4.36E-04	2.96E-03	0.01%	1.50E+02	3.26E-03				
4	2,2,4-Trimethylpentane	1.06E+00	3.11E-01	2.11E+00	0.01%	2.66E+05	2.33E+00				
5	Hexane	1.06E+00	3.09E-01	2.10E+00	0.01%	1.99E+05	2.31E+00				
6	Benzene	1.18E+00	4.24E-02	2.88E-01	0.01%	2.48E+04	3.17E-01	100.01	0.75	133.70	
7	Toluene	1.21E+00	8.43E-02	5.72E-01	0.01%	5.81E+04	6.31E-01				
8	Ethylbenzene	1.17E+00	1.26E-01	8.53E-01	0.01%	9.97E+04	9.39E-01				
9	o-Xylene	1.16E+00	1.26E-01	8.53E-01	0.01%	9.98E+04	9.40E-01				
10	Water	9.42E+02	1.04E-03	7.07E-03	-9.46%	1.40E+02	7.79E-03				
11											
12	Note:										
13	Column B to D: Reiterating Step 3-2(2) and stop when Column E is < 10%.										
14	Column E = (Cloumn C - Column C in step 3_1(previous))/Column C in Step 3_1(previous).										
15	Column F = Column G * MW in Typology table.										
16	Column G = Column C/Column J * 1000.										
17	Column H and I using equation = ΣxiYi, where xi is the molar fraction of component in Column C, Y is the component property of MW and density.										
18	Column J = Column H/Column I.										
19											

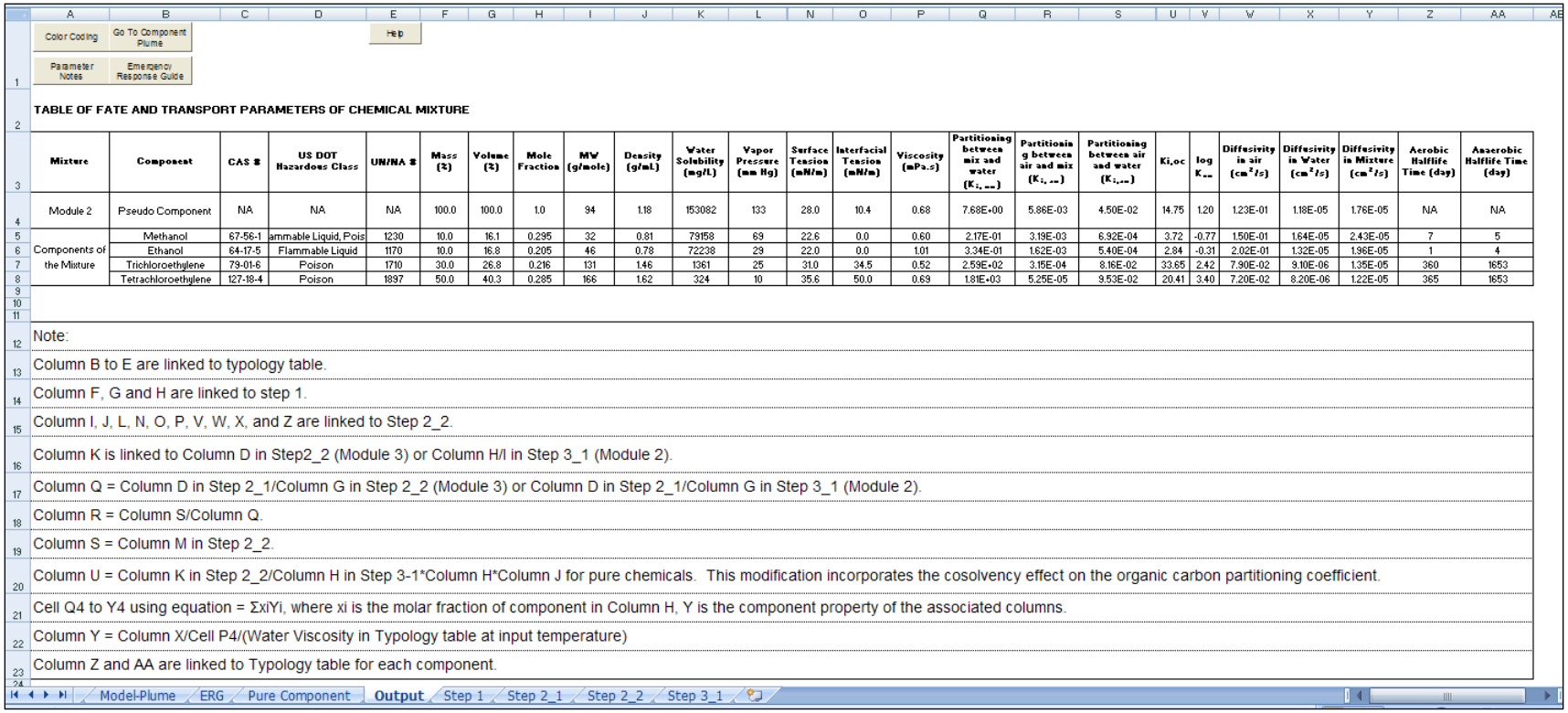
Tool Step 3_1(Final) of Example 1.

Example 2. Chlorinated Solvents

The mixture components and the mass fractions are shown in the Input Interface below.



Input Interface of Example 2.



Color Coding | Go To Component Plume | Help | Parameter Notes | Emergency Response Guide

TABLE OF FATE AND TRANSPORT PARAMETERS OF CHEMICAL MIXTURE

Mixture	Component	CAS #	US DOT Hazardous Class	UN/NA #	Mass (%)	Volume (%)	Mole Fraction	MW (g/mole)	Density (g/mL)	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Partitioning between mix and water ($K_{i,mw}$)	Partitioning between air and mix ($K_{i,am}$)	Partitioning between air and water ($K_{i,aw}$)	Ki,oc	log K_{oc}	Diffusivity in air (cm^2/s)	Diffusivity in Water (cm^2/s)	Diffusivity in Mixture (cm^2/s)	Aerobic Halflife Time (day)	Anaerobic Halflife Time (day)
Module 2	Pseudo Component	NA	NA	NA	100.0	100.0	1.0	94	1.18	153082	133	28.0	10.4	0.68	7.68E+00	5.86E-03	4.50E-02	14.75	1.20	1.23E-01	1.18E-05	1.76E-05	NA	NA
Components of the Mixture	Methanol	67-56-1	ammable Liquid, Pois	1230	10.0	16.1	0.295	32	0.81	79158	69	22.6	0.0	0.60	2.17E-01	3.19E-03	6.92E-04	3.72	-0.77	1.50E-01	1.64E-05	2.43E-05	7	5
	Ethanol	64-17-5	Flammable Liquid	1170	10.0	16.8	0.205	46	0.78	72238	29	22.0	0.0	1.01	3.34E-01	1.62E-03	5.40E-04	2.84	-0.31	2.02E-01	1.32E-05	1.96E-05	1	4
	Trichloroethylene	79-01-6	Poison	1710	30.0	26.8	0.216	131	1.46	1361	25	31.0	34.5	0.52	2.59E+02	3.15E-04	8.16E-02	33.65	2.42	7.90E-02	9.10E-06	1.35E-05	360	1653
	Tetrachloroethylene	127-18-4	Poison	1897	50.0	40.3	0.285	166	1.62	324	10	35.6	50.0	0.69	1.81E+03	5.25E-05	9.53E-02	20.41	3.40	7.20E-02	8.20E-06	1.22E-05	365	1653

Note:

Column B to E are linked to typology table.

Column F, G and H are linked to step 1.

Column I, J, L, N, O, P, V, W, X, and Z are linked to Step 2_2.

Column K is linked to Column D in Step2_2 (Module 3) or Column H/I in Step 3_1 (Module 2).

Column Q = Column D in Step 2_1/Column G in Step 2_2 (Module 3) or Column D in Step 2_1/Column G in Step 3_1 (Module 2).

Column R = Column S/Column Q.

Column S = Column M in Step 2_2.

Column U = Column K in Step 2_2/Column H in Step 3-1*Column H*Column J for pure chemicals. This modification incorporates the cosolvency effect on the organic carbon partitioning coefficient.

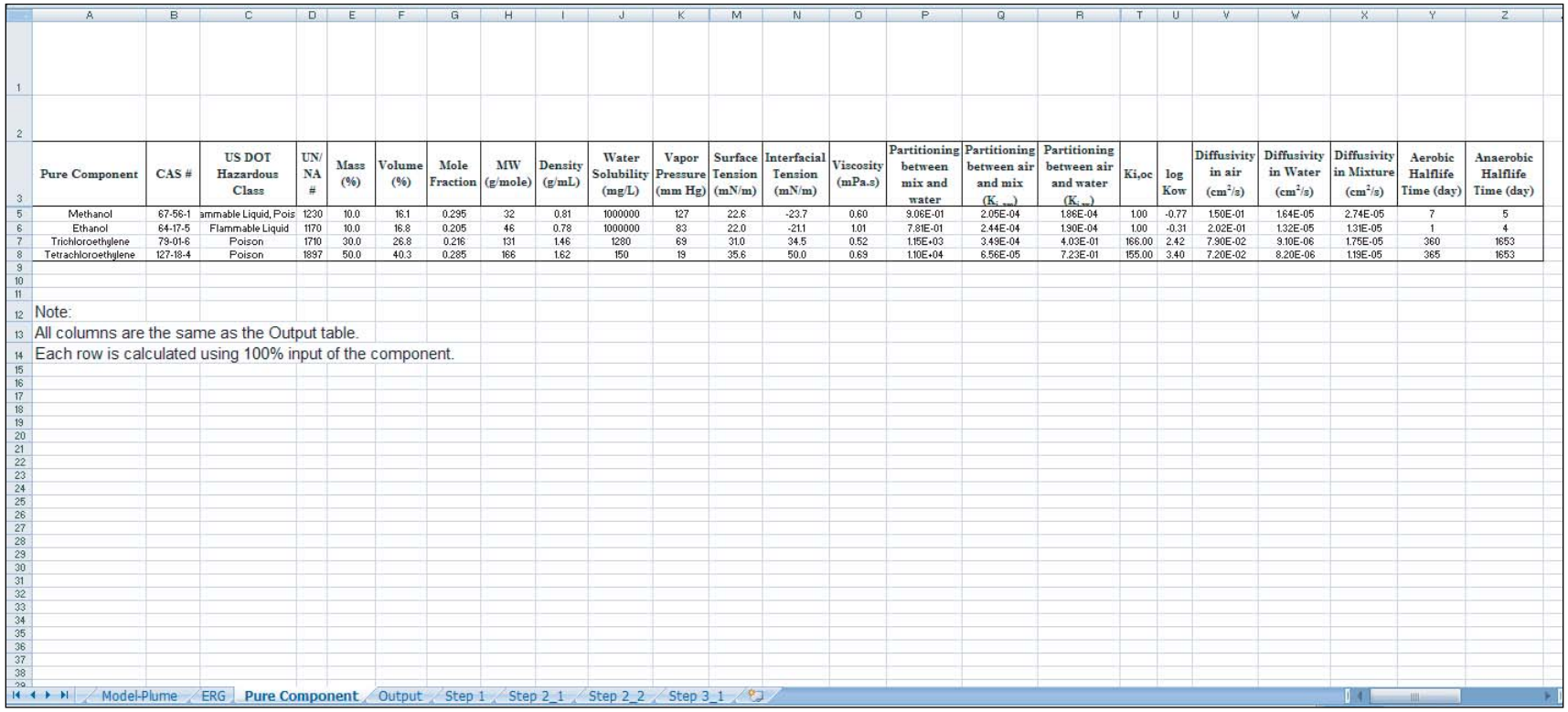
Cell Q4 to Y4 using equation = ΣxiYi, where xi is the molar fraction of component in Column H, Y is the component property of the associated columns.

Column Y = Column X/Cell P4/(Water Viscosity in Typology table at input temperature)

Column Z and AA are linked to Typology table for each component.

Model-Plume | ERG | Pure Component | Output | Step 1 | Step 2_1 | Step 2_2 | Step 3_1

Output Table of Example 2.



Pure Component	CAS #	US DOT Hazardous Class	UN/NA #	Mass (%)	Volume (%)	Mole Fraction	MW (g/mole)	Density (g/mL)	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Partitioning between mix and water	Partitioning between air and mix ($K_{i,am}$)	Partitioning between air and water ($K_{i,aw}$)	Ki,oc	log Kow	Diffusivity in air (cm^2/s)	Diffusivity in Water (cm^2/s)	Diffusivity in Mixture (cm^2/s)	Aerobic Halflife Time (day)	Anaerobic Halflife Time (day)
Methanol	67-56-1	ammable Liquid, Pois	1230	10.0	16.1	0.295	32	0.81	1000000	127	22.6	-23.7	0.60	9.06E-01	2.05E-04	1.86E-04	1.00	-0.77	1.50E-01	1.64E-05	2.74E-05	7	5
Ethanol	64-17-5	Flammable Liquid	1170	10.0	16.8	0.205	46	0.78	1000000	83	22.0	-21.1	1.01	7.81E-01	2.44E-04	1.90E-04	1.00	-0.31	2.02E-01	1.32E-05	1.31E-05	1	4
Trichloroethylene	79-01-6	Poison	1710	30.0	26.8	0.216	131	1.46	1280	69	31.0	34.5	0.52	1.15E+03	3.49E-04	4.03E-01	166.00	2.42	7.90E-02	9.10E-06	1.75E-05	360	1653
Tetrachloroethylene	127-18-4	Poison	1897	50.0	40.3	0.285	166	1.62	150	19	35.6	50.0	0.69	1.10E+04	6.56E-05	7.23E-01	155.00	3.40	7.20E-02	8.20E-06	1.19E-05	365	1653

Note:
All columns are the same as the Output table.
Each row is calculated using 100% input of the component.

Model-Plume | ERG | Pure Component | Output | Step 1 | Step 2_1 | Step 2_2 | Step 3_1

Pure Component Output Table of Example 2.

	A	B	C	D	E	F	G	H
1	**Step 1. Inputs and conversions**							
2	Compound	CAS #	Mass %	mass/density	Vol. %	mass/MW	Mole fraction	
3	Methanol	67-56-1	10.0	12.346	16.145	0.312	0.295	
4	Ethanol	64-17-5	10.0	12.821	16.766	0.217	0.205	
5	Trichloroethylene	79-01-6	30.0	20.489	26.794	0.228	0.216	
6	Tetrachloroethylene	127-18-4	50.0	30.813	40.295	0.302	0.285	
7	Total		100	76	100	1.059	1.00	
8	Temperature	°C	20					
9		K	293					
10		°F	68					
11								
12								
13								
14	Note:							
15	Column C: Red color highligthed are the input data of the mixture.							
16	Temperature is an input parameter too, which will be used in viscosity and diffusion coefficient calculation.							
17	Column D = Column C/density in typology table.							
18	Column E = Column D/Cell D7*100.							
19	Column F = Column C/molecular weight in typology table.							
20	Column G = Column F/Cell F7*100.							
21								

Step 1 of Example 2.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	**Step 2_1. Mixture Phase Properties**																
2	Compound	CAS #	Mole fraction in NAPL	Molar Concentration (mole/L)	MW (g/mole)	Density (g/ml)	Molar Volume (ml)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Activity Coefficient in mix	Individual Solubility (mg/L)	Total Solubility (mg/L)	Individual Vapor Pressure (mm Hg)	Total Vapor Pressure (mm Hg)	Partitioning between mix and water (Ki,mw)	
3	Methanol	67-56-1	0.295	3.671	94.43	1.18	80.28	27.99	10.37	0.68	1.84E+00	5.41E+05	894068	6.87E+01	133	2.17E-01	
4	Ethanol	64-17-5	0.205	2.553							1.72E+00	3.52E+05		2.92E+01		3.34E-01	
5	Trichloroethylene	79-01-6	0.216	2.686							1.71E+00	4.73E+02		2.55E+01		7.47E+02	
6	Tetrachloroethylene	127-18-4	0.285	3.547							1.81E+00	7.74E+01		9.55E+00		7.60E+03	
7																	
8																	
9	Note:																
10	Column C = Column G in Step 1.																
11	Column D = Column C/Column G*1000.																
12	Column E to I using equation = ΣxiYi, where xi is the molar fraction of component I, Y is the component property of MW, density, molar volume, surface tension and interfacial tension.																
13	Column J using equation = $(\Sigma xi(Yi)^{1/n})^n$, where xi is the molar fraction of component I, n is the total component number, Yi is the component viscosity calculated using different equations for each group chemcicals (Equation 12 in the report).																
14	Columnu K is the activity coefficiency of component I in the mixture calculated using XLUNIFAC with the input of component molar fraction and the group info in typology table (Column U to AJ), using input temperate 293 K.																
15	Column L will be γi*xi*Si, γi is the activity coef in column K, Si is the puer compound solubility in typolgy Table Column M.																
16	Column M is the sum of Column L.																
17	Column N will be γi*xi*VPi, γi is the activity coef in column K, Vpi is the puer compound vapor pressure in typolgy Table Column K.																
18	Column O is the sum of Column N.																
19	Column P = Column D/ Column F in Step 2_2.																

Step 2_1 of Example 2.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	**Step 2_2. Aqueous Phase Properties**														
2	Compound	CAS #	Mole fraction in NAPL	Solubility (mg/L)	Solubility (mole/L)	Solubility (mole fraction)	Diffusity in Air (cm^2/s)	Diffusity in Water (cm^2/s)	Aerobic Half-life time (days)	Anaerobic Half-life time (days)	Partitioning between organic carbon and water (Ki,oc)	Henry's Law Constant (atm-m^3/mole)	Partitioning between mix and water (Ki,mw)	Partitioning between air and water (Ki,aw)	
3	Methanol	67-56-1	0.295	5.41E+05	2.47E+00	2.11E-01	1.50E-01	1.64E-05	7.00E+00	5.00E+00	1.00E+00	4.55E-06	2.17E-01	1.86E-04	
4	Ethanol	64-17-5	0.205	3.52E+05	1.57E+00	9.54E-02	2.02E-01	1.32E-05	1.10E+00	4.30E+00	1.00E+00	4.66E-06	3.34E-01	1.90E-04	
5	Trichloroeth	79-01-6	0.216	4.73E+02	1.04E-02	4.49E-05	7.90E-02	9.10E-06	3.60E+02	1.65E+03	1.66E+02	9.85E-03	7.47E+02	4.03E-01	
6	Tetrachloro	127-18-4	0.285	7.74E+01	1.96E-03	5.82E-06	7.20E-02	8.20E-06	3.65E+02	1.65E+03	1.55E+02	1.77E-02	7.60E+03	7.23E-01	
7	Water														
8															
9	Note:														
10	Column C = Column G in Step 1.														
11	Column D: solubility = γi*xi*Si = ColumnC*"Setp2_1"column K*"typology"Column M.														
12	Column E = Column D/"typology" Column G.														
13	Column F = Column E/(55.6+the sum of Column E). Here assume 1:1 NAPL to Water volume ratio. With the adjust of the ratio, the calculation will be different.														
14	Column G to L are the columns in typology table.														
15	Column M = Column P in Step 2_1.														
16	Column N = Column M*40.8745 to convert Hendy's Law Constant to unitless.														
17	If there are no components in the mixture with parameters in Column AZ and BA (cosolvency parameter) in the typology table, this step is the final step of Module 3. If there are any components in the mixture with cosolvent parameters, further solubility and organic carbon partitioning coefficient calculations in step 3-1.														
18															

Step 2_2 of Example 2.

	A	B	C	D	E	F	G	H	I	J
1	**Step 3_1. Aqueous Phase Properties**									
2	Compound	CAS #	Mole fraction	Water Solubility (mole/L)	Volume (cm^3)	Volume fraction	Final Water Solubility (mole/L)	Final Water Solubility (mg/L)	Total Solubility (mg/L)	
3	Methanol	67-56-1	0.295	3.01570	107	8.73E-02	2.47E+00	7.92E+04	153082	
4	Ethanol	64-17-5	0.205	1.91412	113	9.25E-02	1.57E+00	7.22E+04		
5	Trichloroethylene	79-01-6	0.216	0.00359	0.320	2.62E-04	1.04E-02	1.36E+03		
6	Tetrachloroethylene	127-18-4	0.285	0.00047	0.047	3.83E-05	1.96E-03	3.24E+02		
7	Water	7732-18-5		55.6	1000.8	8.20E-01				
8										
9	Note:									
10	Column C = Column G in Step 1.									
11	Column D = 'Step 2-1'!D3/(1+'Step 2-1'!P).									
12	Column E = Column D*Typology!U.									
13	Column F is the fraction based on Column E. Equation 28 b1 in the report.									
14	Column G is calculated based on cosolvent log linear relationship: =10^(LOG(CloumnD)+$F$3*(Typology!$AZ$4*Typology!T4+Typology!$BA$4)+$F$4*(Typology!$AZ$5*Typology!T4+Typology!$BA$5). Equation 28, 28 a, 28b, 28 c in the report.									
15	Column H = Column G/Column G in Typology.									
16	Column I is the sum of Column H.									
17										

Step 3_1 of Example 2.

APPENDIX M

User Operational Manual

TABLE OF CONTENTS

1. REQUIREMENTS

- Excel (Program tested using versions 2003 and 2007)
- A Microsoft Windows PC (Currently not available in Mac)
- At least 256 MB of system RAM
- Recommended: 3.0+ Ghz CPU (2.0+ Ghz Parallel or Multi-core CPU)

2. STARTING THE PROGRAM

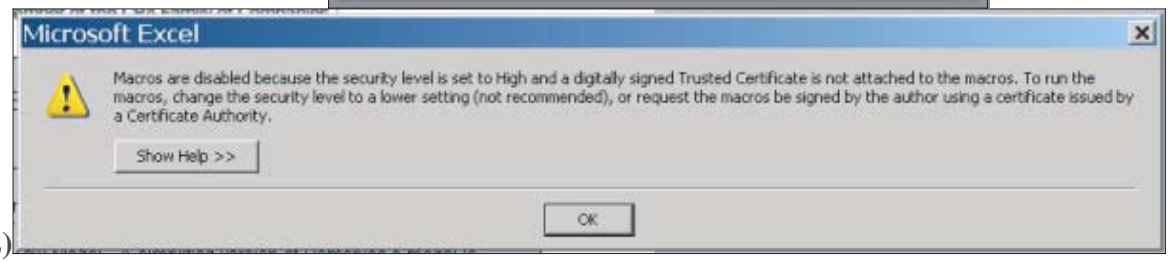
The tool is designed in Excel using Visual Basic for Application (VBA), requiring Excel Macros to operate. Macros are written inside the tool to operate the toolbar buttons or help icons and repeat the steps of common calculations.

2.1. Excel 2003

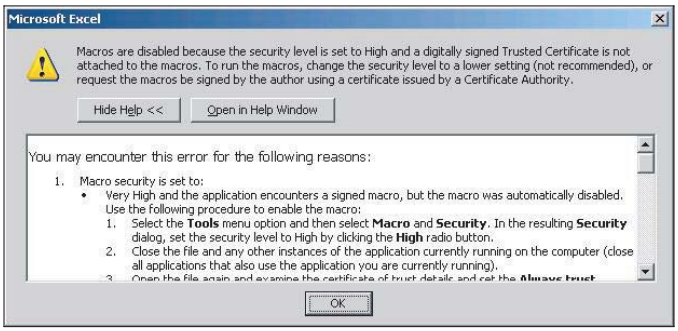
Depending on your macro security settings, you may see one of the following three messages when you open the Excel file:

1)

2)

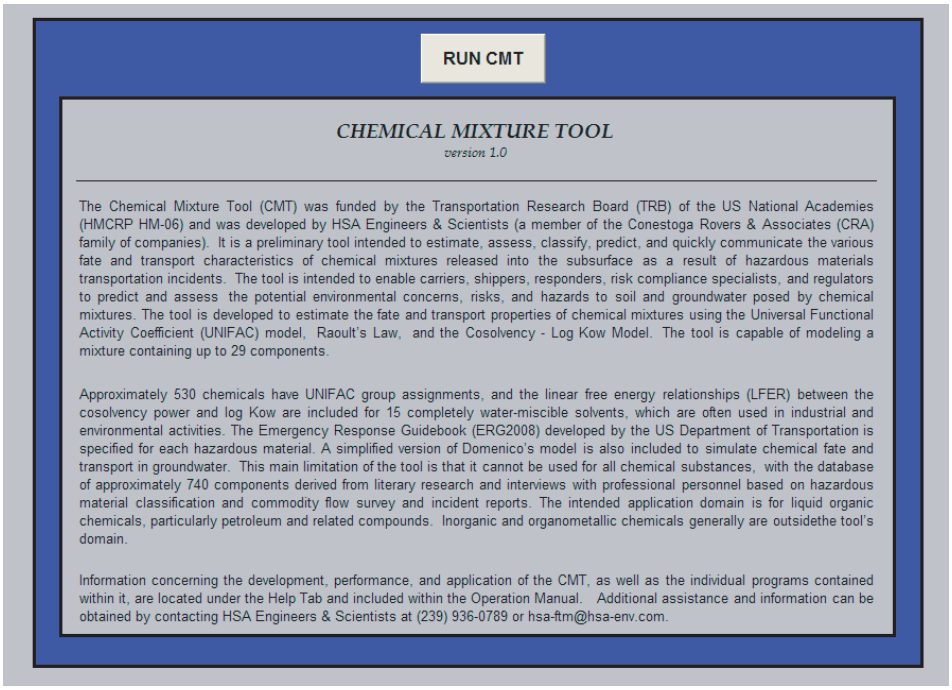


3)



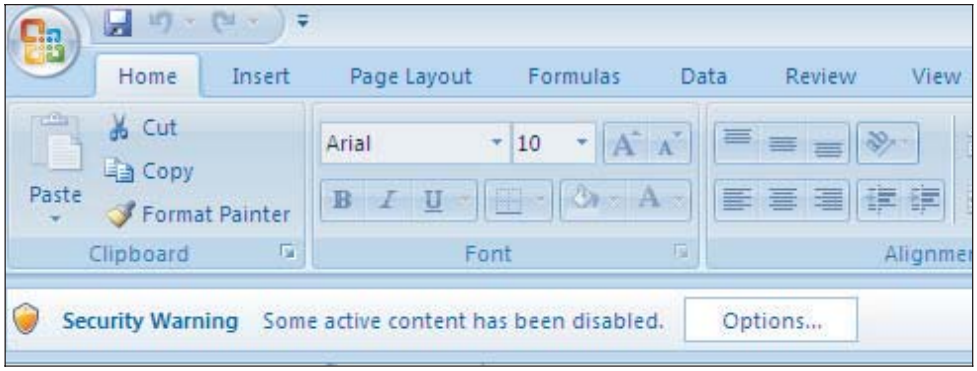
If you see the first dialog box, please select the "Enable Macros" button and the tool will initialize. The second and the third dialogue boxes will require you to reduce your security level in Excel (Please see the troubleshooting section 5.1 for detailed assistance). Select the following: "Menu," then "Tools," then "Options," then "Security," and then click on "Macro Security." Lower the security level to "Medium or Low." This step requires that the user restart the Excel Software and reopen the Chemical Mixture Tool.

Once the macro has been allowed to run according to the instructions above, the tool will show the front page in Excel as shown below. Clicking the "RUN CMT" button will show the input form and continue the tool process.



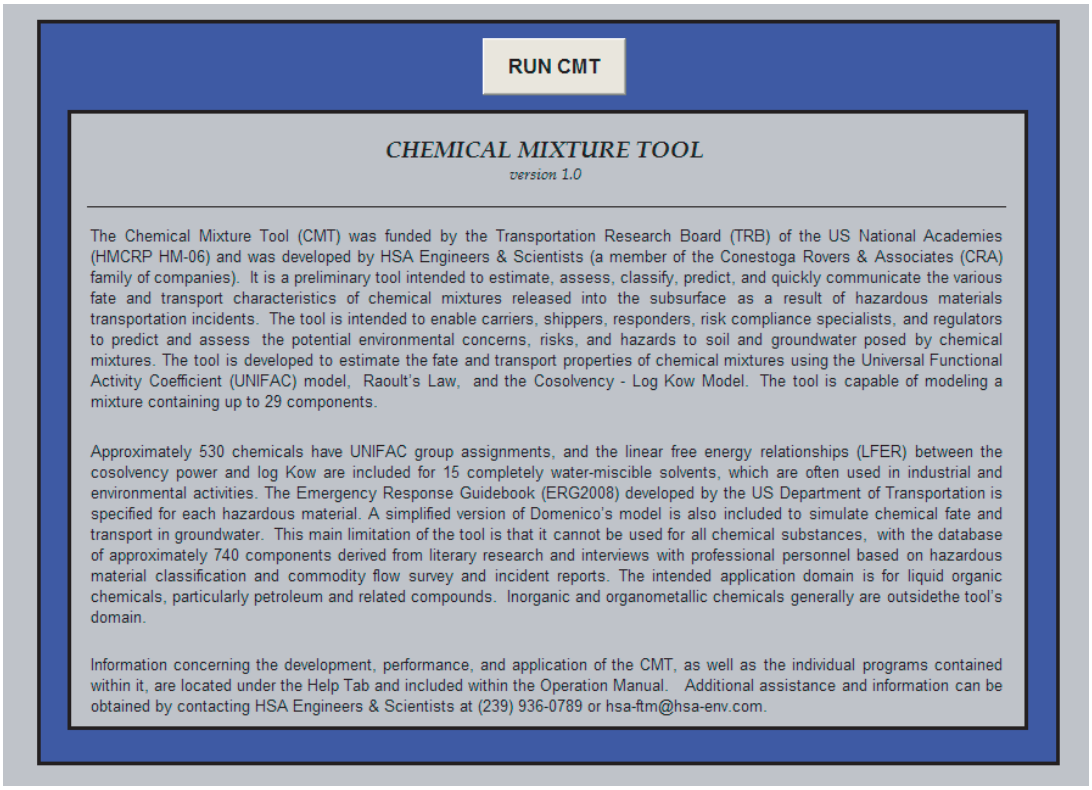
2.2. Excel 2007

Depending on your macro security settings, you may see the following warning when you open the Excel file:



Click the "Options" button, and then choose the option: "Enable this content." Click "Okay." If you do not see this item and did not receive the above warning, your security settings are too strict (please refer to the troubleshooting section 5.1 for assistance).

Once the macro has been allowed to run per the above instructions, you should see the tool front page in Excel as below. Clicking the "RUN CMT" button will show the input form and continue the tool process.

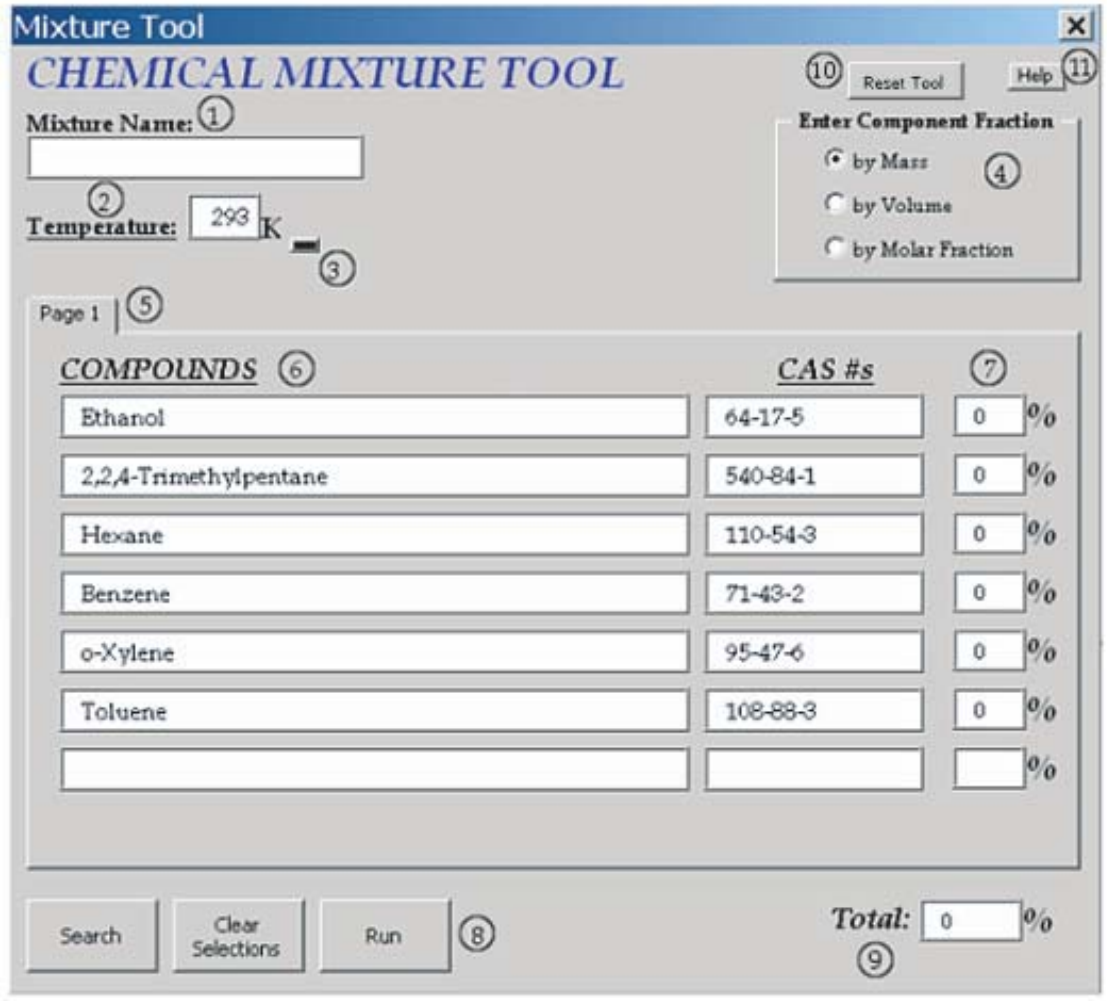


3. TOOL INPUT AND EXECUTION

3.1. Tool Input Parameters

Interface and Help Button

On the Tool input interface, click the "Help" button on the right top corner and the Help menu will open to illustrate the input interface functions as shown below.

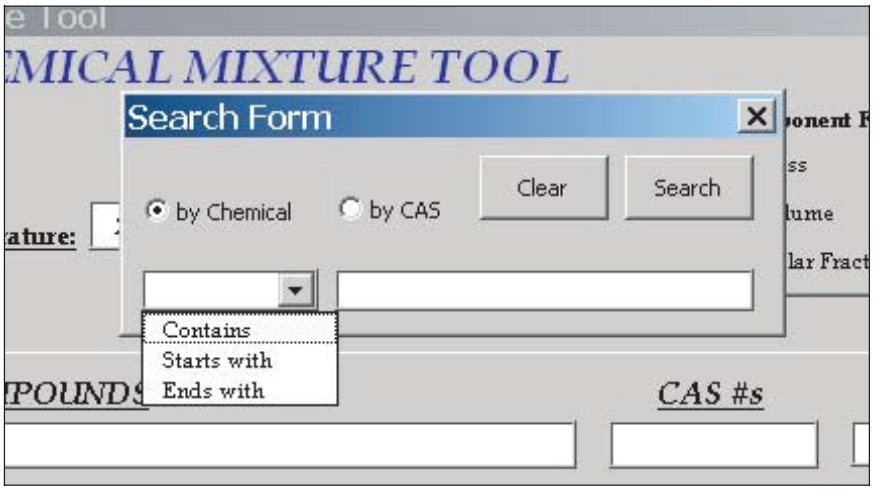


1) Mixture Name: Enter the mixture name. The default is "Mixture, m."
2) Temperature (Required): Enter the desired temperature.
3) Temperature Unit: Unit of associated temperature. Default is Kelvin.
4) Component Fraction: Method by which ratio of components will be defined.
5) Page Selection: Once a certain number of components have been entered, additional pages will appear and can be toggled between here.
6) Component Input: Enter the component by either name or CAS number.
7) Ratio of Components: Based on (4), enter the amount of each component in the mixture.
8) Function Buttons:
1. Search: Allows a search of the registry by CAS or name (details below).
2. Clear Selections: Resets the form.
3. Run: Begins the calculation process and produces output.

9) Total: Displays the sum of (7). Must be 100 % by Mass or Volume; 1.0 by Molar Fraction for the tool to proceed.
10) Reset Tool: Click to reset the tool at various mixture-water ratios.

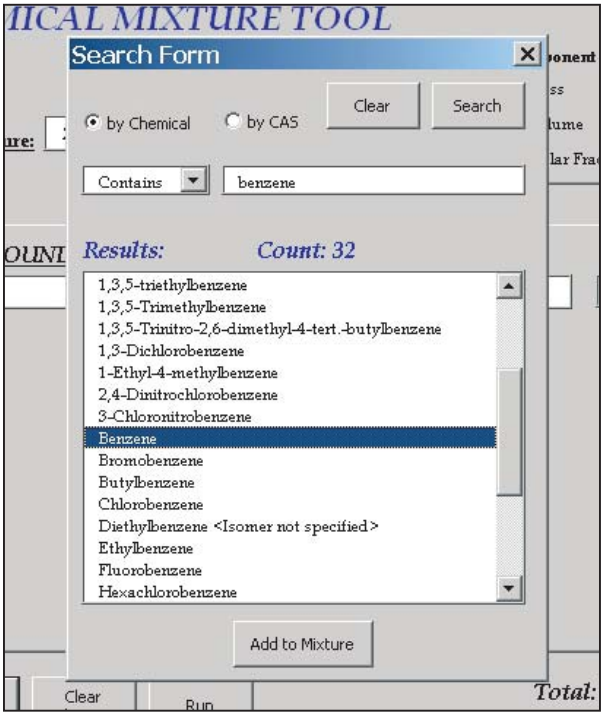
11) Help: Illustrate the Input Interface and functions.

Searching the Compound Registry



When the "Search" button is clicked on the main form, the above window will open. Using the radio buttons, select which registry you would like to search. The drop down menu will allow you to limit the way in which you search the registry to items which begin with your data entry, items which end with your data entry, or items which contain your data entry at any point.

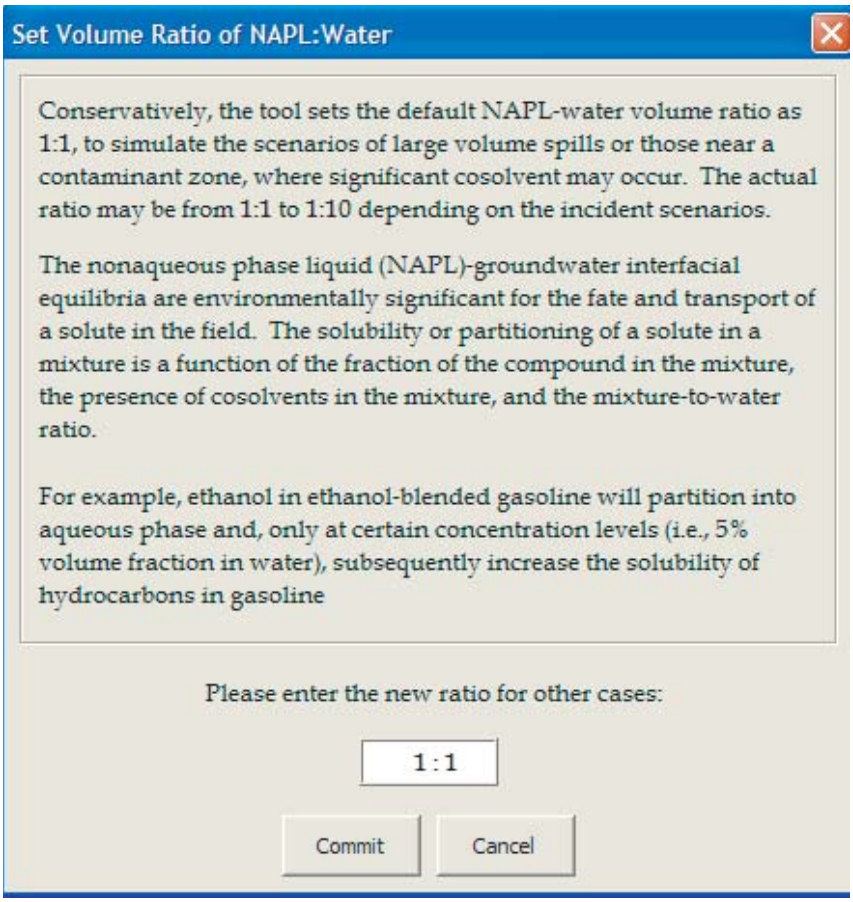
After completing it, click the "Search" button on this form, and results will be displayed (note: entering nothing in the input box will result in all items in the registry being returned alphanumerically).



To return a component to the main form, select it from the resulting list and click the "Add to Mixture" button. Only one anonym of a chemical is in the tool database, therefore, searching by CAS# will be the most convenient means to find an input component.

If you do not see the component you are looking for, you may use the "Clear" button to reset this form and try again. If a desired chemical cannot be found either by chemical name or CAS# search, the desired chemical is not in the tool database.

3.2. Reset the Tool



The nonaqueous phase liquid (NAPL)-groundwater interfacial equilibria are environmentally significant for the fate and transport of a solute in the field. The solubility or partitioning of a solute in a mixture is a function of the fraction of the compound in the mixture, the presence of cosolvents in the mixture, and the mixture-to-water ratio. For example, ethanol in ethanol-blended gasoline will partition into aqueous phase and, only at certain concentration levels (i.e., 5% volume fraction in water), subsequently increase the solubility of hydrocarbons in gasoline. Conservatively, the tool sets the default NAPL-water volume ratio as 1:1 to simulate the scenarios of large volume spills or the near contaminant zone, where significant cosolvent may occur. The actual ratio may range from 1:1 to 1:10 depending on the incident scenarios. Every time when the tool is opened, it is automatically reset to a 1:1 ratio. Please enter the new ratio for other cases.

3.3. Running the Tool

After the "Run" button is clicked on the main form, a series of simple checks will be performed to ensure the input is complete. If it is, an action bar and series of status messages will appear to inform you of the current action the tool is taking and to let you know that it is working.

This may take several minutes based on the number of components, path through the tool, and CPU speed of your computer.

4. OUTPUT AND INTERPRETATION

After the tool has finished running, an output interface will be displayed as shown as below. The default output page will provide a summary table of the fate and transport property parameters of your input mixture as well as a number of calculated values further to the right of what is shown here. In addition, there are four buttons (1 through 4) and a "Help" button (5) that will display a basic summary of each button's function from within the tool itself.

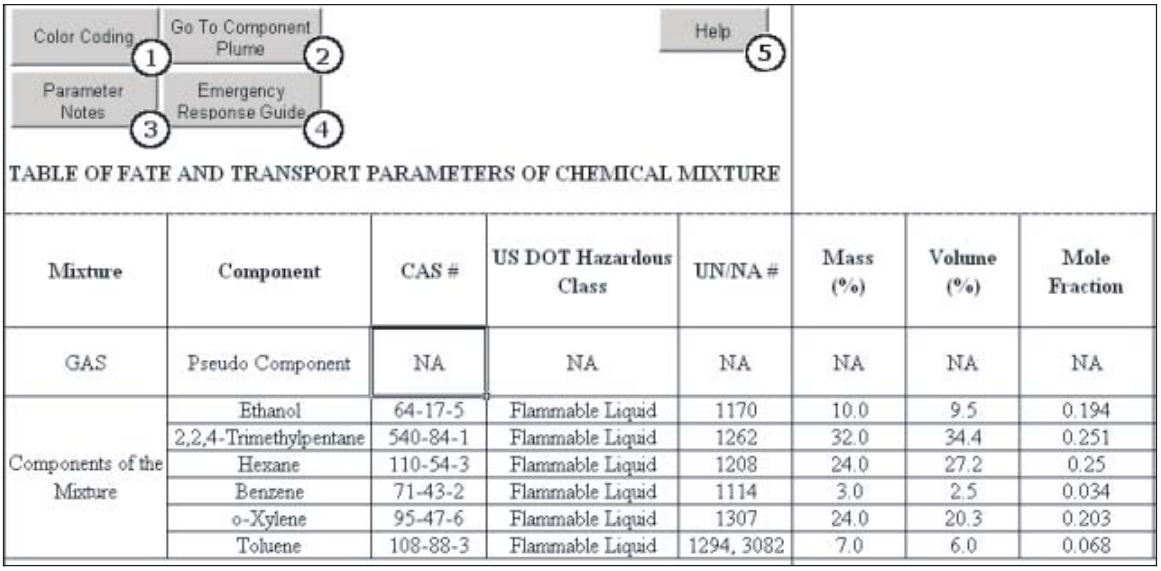


TABLE OF FATE AND TRANSPORT PARAMETERS OF CHEMICAL MIXTURE

Mixture	Component	CAS #	US DOT Hazardous Class	UN/NA #	Mass (%)	Volume (%)	Mole Fraction
GAS	Pseudo Component	NA	NA	NA	NA	NA	NA
Components of the Mixture	Ethanol	64-17-5	Flammable Liquid	1170	10.0	9.5	0.194
	2,2,4-Trimethylpentane	540-84-1	Flammable Liquid	1262	32.0	34.4	0.251
	Hexane	110-54-3	Flammable Liquid	1208	24.0	27.2	0.25
	Benzene	71-43-2	Flammable Liquid	1114	3.0	2.5	0.034
	o-Xylene	95-47-6	Flammable Liquid	1307	24.0	20.3	0.203
	Toluene	108-88-3	Flammable Liquid	1294, 3082	7.0	6.0	0.068

4.1. Color Coding

The "Color Coding" button (1) is designed to compare the properties of a component to its pure phase using different colors. Clicking the button will toggle the color coding on and off. The "Color Coding" button (1) will shade parameter Water Solubility through Anaerobic Half-Life time based on the specific parameter in that column in the mixture compared to that same parameter as a pure compound.

- The Lime Green color represents the ratio of the property less than 5.0, which indicates that there are no significant changes in the property of the mixture compared to the pure chemical.
- The Orange color represents the ratio of the property between 5.0 and 10.0, indicating that there are slight changes in the property of the mixture compared to the pure chemical.
- The Red color represents the ratio of the property greater than 10.0, indicating that the chemical mixture may have a dramatic effect on the property of a component.
- The Blue color highlights the major mixture NAPL transport properties in the unsaturated zone.

Return to Table

Help On Output Interface

This output interface presents the fate and transport parameters of the input chemical mixture and its components generated by the Chemical Mixture Tool. In addition, there are four clickable buttons on this interface, which help to interpret the tool results and with the application of the tool results.

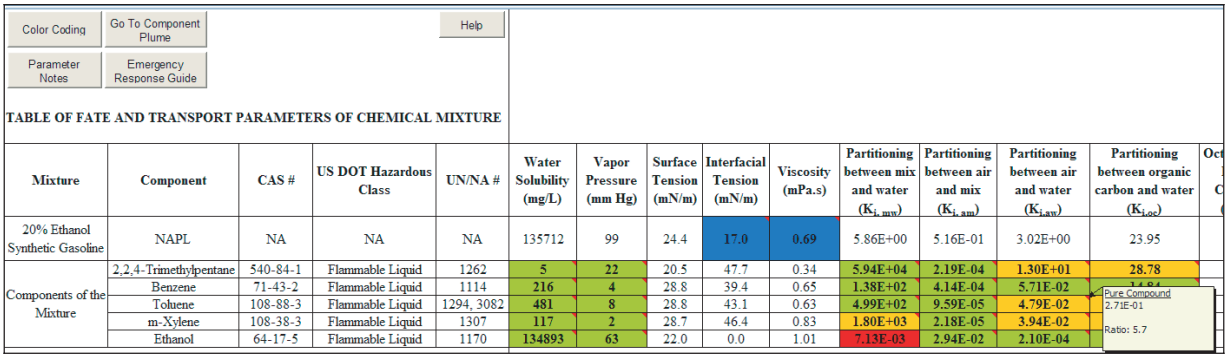
"**Color Coding**" is designed to compare the properties of a component to its pure phase using different colors. Clicking the button will toggle the color coding on and off.

- The Lime color represents the ratio of the property less than 5.0, which indicates that there are no significant changes in the property of the mixture compared to the pure chemical.
- The Orange color represents the ratio of the property between 5.0 and 10.0, indicating that there are slight changes in the property of the mixture compared to the pure chemical.
- The Red color represents the ratio of the property greater than 10.0, indicating that the chemical mixture may have a dramatic effect on the property of a component.
- The Blue color highlights the major mixture NAPL transport properties in the unsaturated zone.

"**Parameter Notes**" is designed to interpret the physical and chemical parameters and terms used in the output table. Click the "Return to Table" button to return to the current output interface.

"**Go To Component Plume**" is designed to simulate a component plume in a saturated groundwater aquifer with default hydrogeologic characteristics. Click on any component then click "Go To Component Plume" and it will take the user to an interface of the Domenico Analytical Model designed by HSA, where a plume of the component is shown with the associated model input parameter (a "Help" button is included to help the users understand how to simulate the fate and transport of a component in groundwater). Clicking the "Return to Table" button will return the user to the current output interface.

"**Emergency Response Guide**" is designed to assign each chemical component an Emergency Response Guidebook (ERG2008), which was developed by the United States Department of Transportation (US DOT). Click on any component then click the "Emergency Response Guide" Button, and it will take the user to the interface of the appropriate emergency response guide according to the US DOT Hazardous Class and United Nations Identification Number (UN#) assigned to the component for proper shipping. If UN# is not available for a chemical, this button will not function. Clicking the "Return to Table" button will take the user to the current output interface.



Color Coding | Go To Component Plume | Help
Parameter Notes | Emergency Response Guide

TABLE OF FATE AND TRANSPORT PARAMETERS OF CHEMICAL MIXTURE

Mixture	Component	CAS #	US DOT Hazardous Class	UN/NA #	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Viscosity (mPa.s)	Partitioning between mix and water ($K_{i,mw}$)	Partitioning between air and mix ($K_{i,am}$)	Partitioning between air and water ($K_{i,aw}$)	Partitioning between organic carbon and water ($K_{i,oc}$)	Oct
20% Ethanol Synthetic Gasoline	NAPL	NA	NA	NA	135712	99	24.4	17.0	0.69	5.86E+00	5.16E-01	3.02E+00	23.95	
Components of the Mixture	2,2,4-Trimethylpentane	540-84-1	Flammable Liquid	1262	5	22	20.5	47.7	0.34	5.94E+04	2.19E-04	1.30E+01	28.78	
	Benzene	71-43-2	Flammable Liquid	1114	216	4	28.8	39.4	0.65	1.38E+02	4.14E-04	5.71E-02		
	Toluene	108-88-3	Flammable Liquid	1294, 3082	481	8	28.8	43.1	0.63	4.99E+02	9.59E-05	4.79E-02		
	m-Xylene	108-38-3	Flammable Liquid	1307	117	2	28.7	46.4	0.83	1.80E+03	2.18E-05	3.94E-02		
	Ethanol	64-17-5	Flammable Liquid	1170	134893	63	22.0	0.0	1.01	7.13E-03	2.94E-02	2.10E-04		

Pure Compound
2.71E-01
Ratio: 5.7

In addition, a note (shown above) will be added to each Orange/Red cell, which will show the associated value when the compound is not mixed as well as the ratio between the two. It should be noted that even though the color change from green to red indicates the severity of the property change of a component in a mixture compared to its pure phase, the red color does not guarantee the mixture is not acceptable considering the uncertainty of the tool.

Notes:

NAPL - Nonaqueous phase liquid. The input mixture considered as a single NAPL compound.
NA - Not available or not known.
CAS # - Chemical Abstract Service registry number, which uniquely identifies chemicals. It is also referred to as CAS RN.
US DOT Hazardous Class - US Department of Transportation hazardous material class or division.
UN/NA # - United Nations or North American identification numbers assigned to each proper shipping.
Mass - The weight percentage of each component in the hazardous material mixture.
Volume - The volume percentage of each component in the hazardous material mixture.
Mole Fraction - The molar fraction of each component in the hazardous material mixture.
MW - The molecular weight of the component, which is unique for each chemical.
Density - Relevant for the upward movement by buoyant force or downward movement by gravitational force of a nonaqueous phase liquid (NAPL).
Water Solubility - The solubility in water at the condition of a 1:1 volume ratio of NAPL to water, which is relevant for the partitioning of a component to various phases.
Vapor Pressure - Relevant for the gaseous partitioning of a component.
Surface tension - NAPL surface tension against air, which is relevant for phase capillarity and the extent of spreading of a liquid to another surface.
Interfacial Tension - The interfacial tension between the mixture and water, which is relevant for the wettability of a component. The less the interfacial tension, the more miscible the NAPL is with water.
Viscosity - Relevant for mobility of a NAPL. The lower the viscosity, the easier the NAPL moves.
$K_{i,mw}$ - Partition coefficient between the mixture and water (molar unit), which is relevant for phase equilibrium and the solubility in water.
$K_{i,am}$ - Partition coefficient between air and the mixture (molar unit), which is relevant for phase equilibrium and the concentration in air.
$K_{i,aw}$ - Partition coefficient between air and water (unitless).
$K_{i,oc}$ - Partition coefficient of a component between organic carbon and water, which is relevant for adsorption of a NAPL to sediment and the retardation factor of a NAPL's travel velocity.
log K_{ow} - Partition coefficient between octanol and water.
D_a - Diffusion coefficient in air, which is relevant for the ease of a molecule to move in air.
D_w - Diffusion coefficient in water, which is relevant for the ease of a molecule to move in water.
D_m - Diffusion coefficient in mixture, which is relevant for the ease of a molecule to move in the mixture.
Aerobic $t_{1/2}$ - The half-life time of a component under aerobic conditions. The smaller the half-life time, the faster the chemical decays.
Anaerobic $t_{1/2}$ - The half-life time of a component under anaerobic conditions.

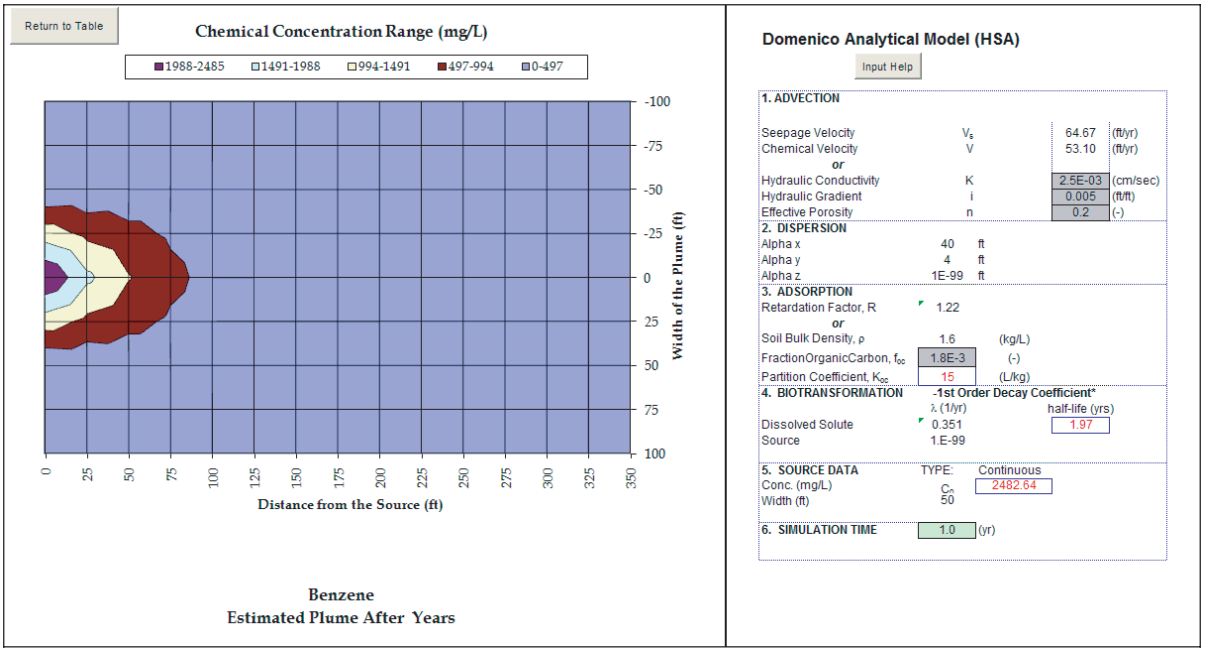
4.2. Parameter Notes

The "Parameter Notes" button (2) is designed to interpret the physical and chemical parameters and terms used in the output table. When this button is selected, a note box will open as below to

interpret the parameters and definitions in the output table. Click the "Return to Table" button to return to the output interface.

4.3. Screening Model

The "Go to Component Plume" button (3) is designed to simulate a component plume in a saturated groundwater aquifer with default hydrogeologic characteristics. Select any component and then click the "Go to Component Plume" button and it will take the user to an interface of the Domenico Analytical Model designed by the research team, where a plume of the component is shown. The default simulation time is one year.



The "Return to Table" button below the plume illustration will return the user to the main output sheet. Located to the right of the plume illustration are the entry parameters used to generate it.

These are the generic parameters, which can be adjusted to fit the specific conditions in question. The concentration, partition coefficient, and half-life are calculated by the mixture tool (blue borders with a red font) and should not be changed. Please use the "Help" button below the input area to access detailed data entry instructions as shown below. Click the "Return to Plume" button to return to the screening model interface.

Return to Plume

Help on How to Run the Screening Model

This Domenico Screening Model is built in the Chemical Mixture Tool to simulate the transport in groundwater using a plume for each component of the input hazardous material. Some of the input parameters of this Screening Model can be modified to represent the site specific conditions, while several parameters are entered directly from the tool results (e.g., organic carbon partition coefficient (K_{oc}), first order degradation half-life time, and solute concentration).

The cell shaded with a green background is the simulation time in years. A time range of 0 - 99 years can be input to simulate the changes of the component plume over time. Increasing the simulation time should lead to a longer plume. No obvious plume changes over the simulation time may indicate the component plume reaches steady state.

The cells highlighted by blue borders and a red font, including organic carbon partition coefficient (K_{oc}), half-life time (yrs), and concentration (mg/L), are solute specific transport parameters. These data represent the properties of the component in the mixture generated from the tool (Output Table). The half-life time is the anaerobic degradation from the output table, which can be adjusted to aerobic half-life time based on the site conditions.

The cells shaded with a grey background are the site hydrogeologic characteristics of the Aquifer (e.g., hydraulic conductivity, hydraulic gradient, and effective porosity), including the following with typical values. These parameters can be adjusted according to the site specific information to run the Screening Model.

Hydraulic Conductivity (K) (cm/sec)

Description	The hydraulic conductivity of the saturated porous medium. The higher the hydraulic conductivity, the more permeable the aquifer.	
Typical Values	Clays:	$<1x10^{-6}$
	Silts:	$1x10^{-6}$ - $1x10^{-3}$
	Silty sands:	$1x10^{-5}$ - $1x10^{-1}$
	Clean sands:	$1x10^{-3}$ - 1
	Gravels:	> 1
Default Value		2.50E-03

Hydraulic Gradient (i) (ft/ft)

Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table. The bigger the hydraulic gradient leads to faster groundwater flow for a certain aquifer media.
Typical Values	0.0001 - 0.05
Default Value	0.005

Effective Porosity (n) (unitless)

Description	Dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix, also called "Open Porosity", referring to the fraction of the total volume of a aquifer in which fluid flow is effectively taking place.	
Typical Values:	Clay	0.01-0.20
	Silt	0.01-0.30
	Fine Sand	0.10-0.30
	Medium Sand	0.15-0.30
	Coarse Sand	0.20-0.35
	Gravel	0.10-0.35
	Sandstone	0.005-0.10
	Unfract. Limestone	0.001-0.05
	Fract. Granite	0.00005-0.01
Default Value		0.20

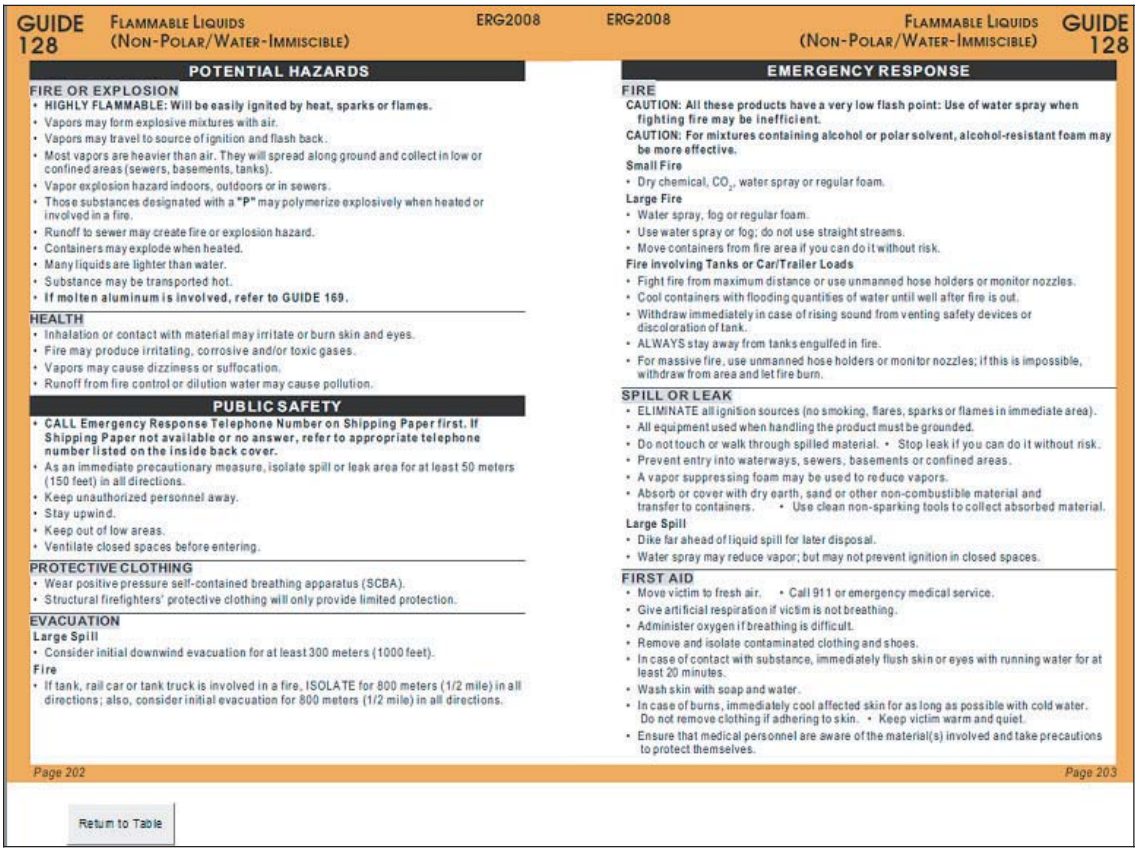
Fraction Organic Carbon (f_{oc}) (unitless)

Description	The fraction of the aquifer soil matrix comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix. The fraction organic carbon value should be measured if possible by collecting a sample of aquifer material from an uncontaminated zone and performing a laboratory analysis.
Typical Values	0.0002 - 0.02
Default Value	0.0018

Default Values & Adjustments	Commonly used values for silts and sands are set as default input for hydrogeologic parameters. These parameters can be adjusted according to the site specific information to run the screening model.

4.4. Emergency Response Guidebook (ERG 2008)

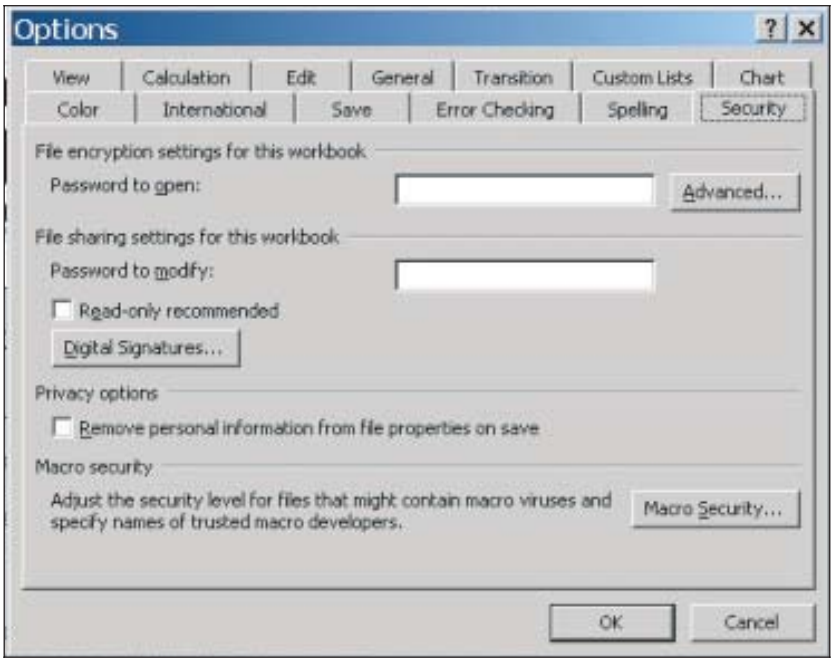
The "Emergency Response Guide" button (4) is designed to assign each chemical component an Emergency Response Guidebook (ERG 2008), which was developed by the United States Department of Transportation (U.S. DOT). Select one component and click the "Emergency Response Guide" button, and it will take the user to the interface of appropriate emergency response guides according to the U.S. DOT Hazardous Class and United Nations Identification Number (UN#) assigned to the component for proper shipping as shown below. Clicking the "Return to Table" button at the bottom of the ERG will take the user to the current output interface.



5. TROUBLESHOOTING

5.1. Adjusting Macro Security

Excel 2003:



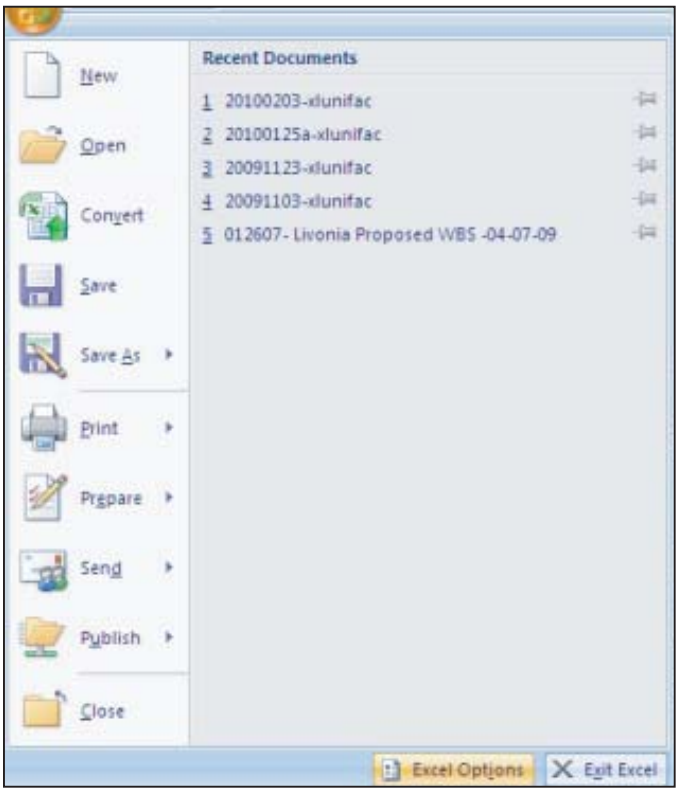
From the menu, select "Tools" then "Options" to open the above screen. Select the Security Tab from the groups at the top of this menu, and then click the "Macro Security" button from the bottom of the Security Tab. This will open the following menu:

Here the user can change the security settings. "Medium" is the recommended setting which will result in the prompt mentioned above. A higher security setting will not allow the tool to run, and a lower security setting may allow potentially malicious macros to run without prompting, if the user is concerned.

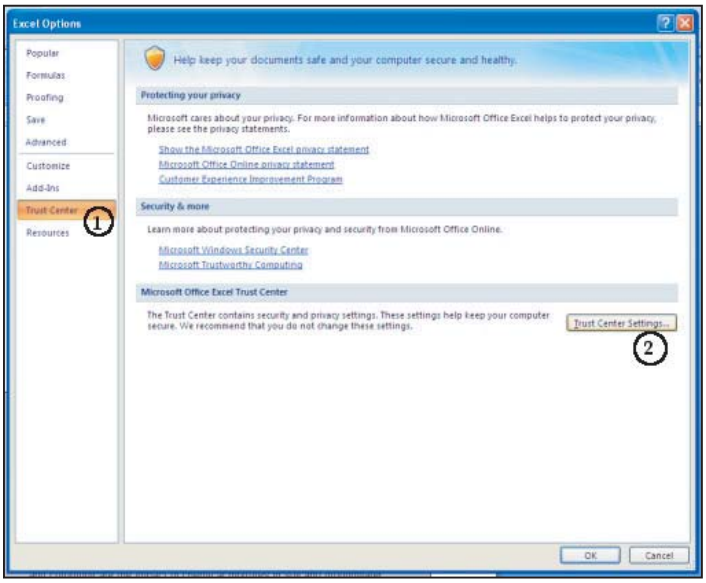
Once this setting has been changed, the tool must be closed and re-opened in order to proceed.

Excel 2007:

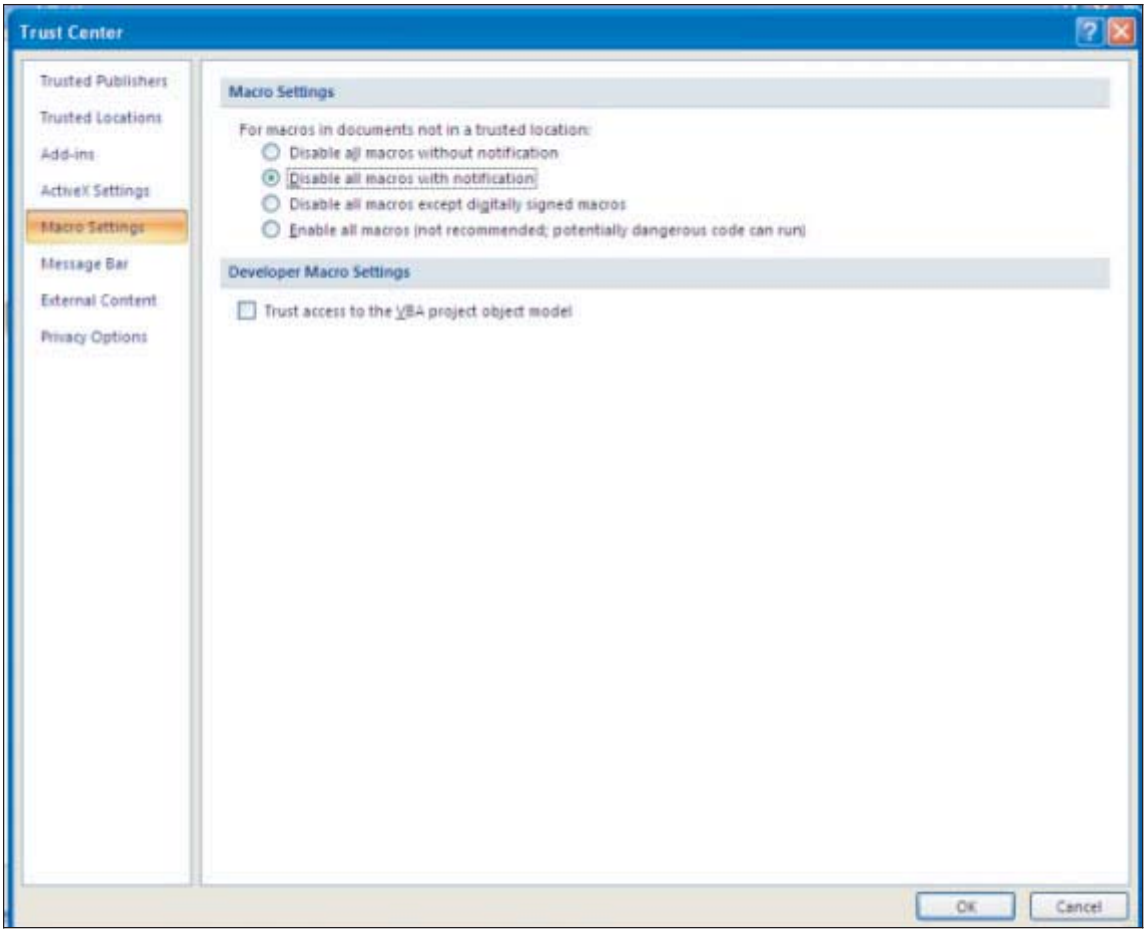
Using the Office button (pictured to left) will show the following:



Here, the user will select the highlighted button at the bottom (Excel Options), which will allow access to a number of application settings.



On the next window, navigate first to the “Trust Center” (1), and then open the “Trust Center Settings” (2).

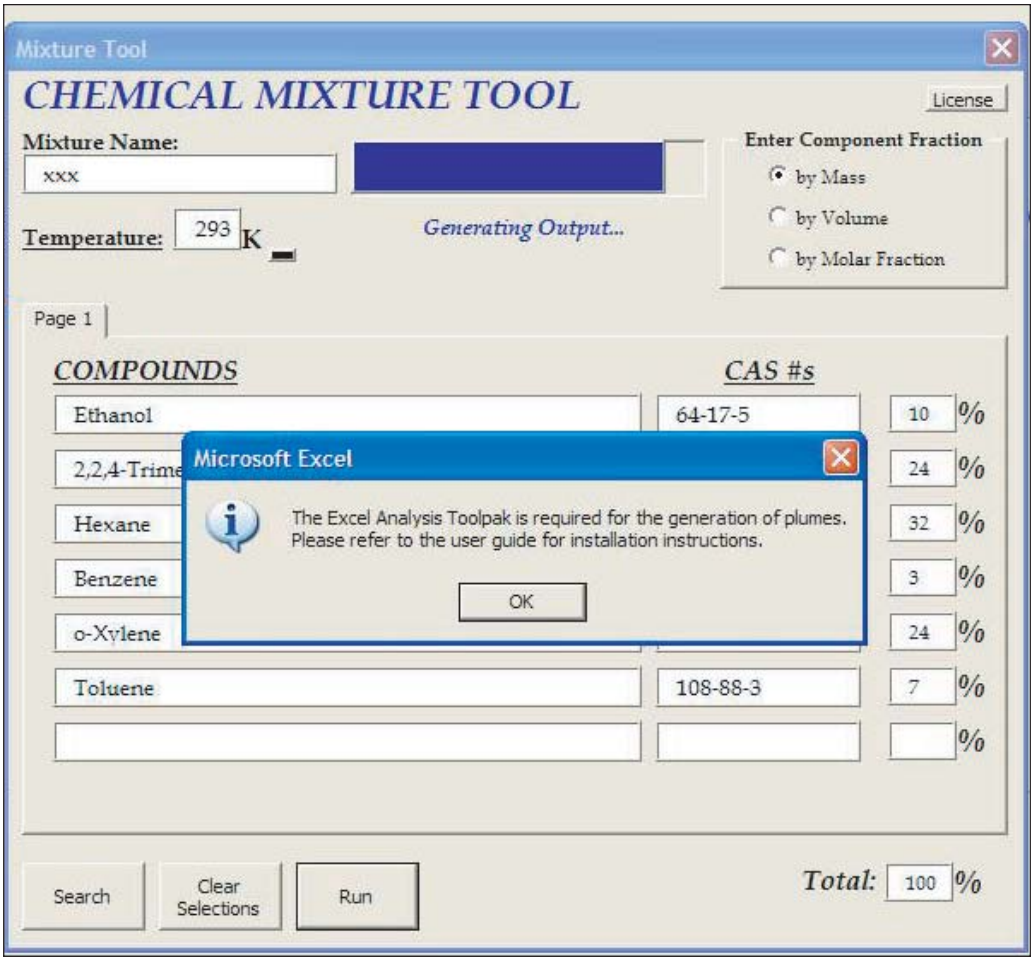


Finally, the user can change the security setting under "Macro Settings." Selecting "Disable all macros with notification" is recommended and will result in the same behavior described in this document. Anything higher will prevent the tool from running, while anything lower will permit potentially malicious macros to run without prompt.

Once this setting has been changed, the tool must be closed and re-opened in order to proceed.

5.2. Adding the ERROR Function for Screening Model

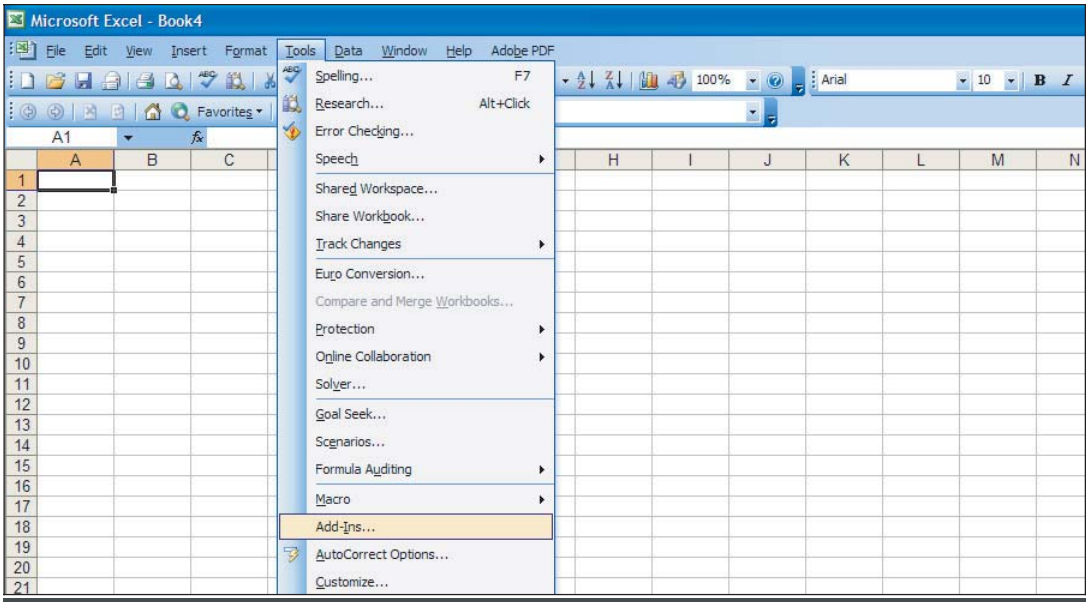
The tool will automatically turn on the Analysis Toolpak in Excel as an Add-in to run the screening model. If it fails to turn on the ERROR Function in the Analysis Toolpak, a note will show as pictured below. If this function is not available, the data source calculations for the plume will result in "#VALUE!" Or "#NAME?" errors, and no chemical plume will be shown.

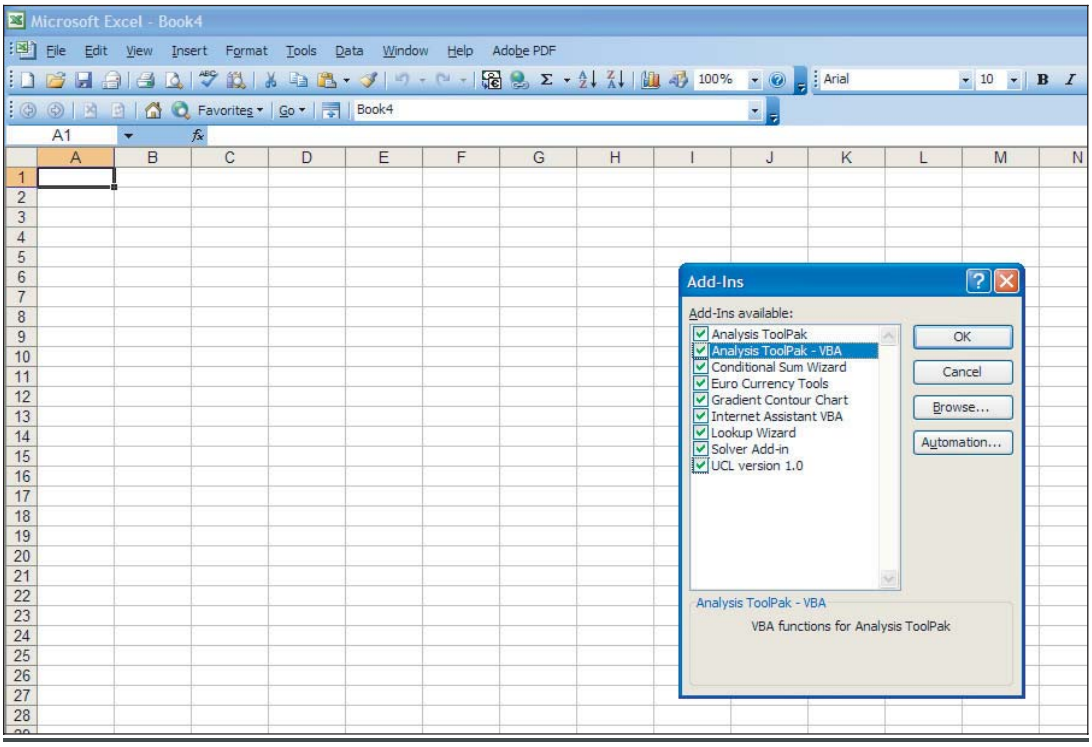


Next, install and load the Analysis ToolPak add-in following the instructions on the following page.

Excel 2003:

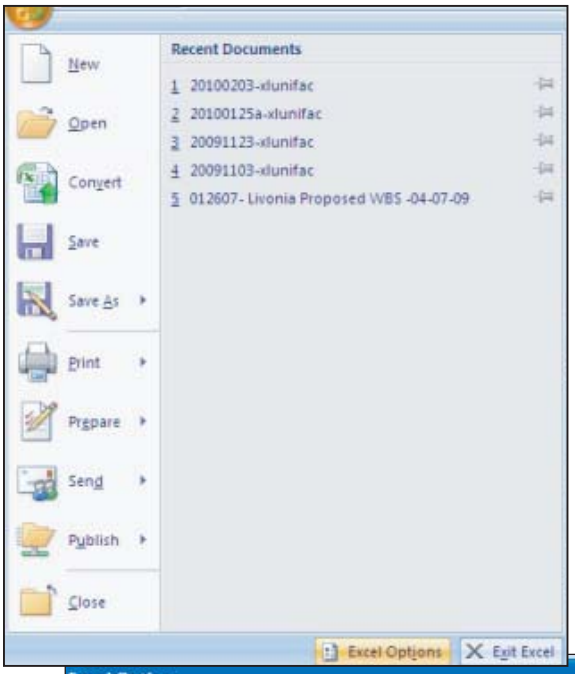
From the menu, select “Tools” and then “Add-Ins” to open the second screen below. From this menu, check the boxes next to both “Analysis ToolPak” and “Analysis ToolPak – VBA,” then click OK. Close Excel and reopen it, then run the Chemical Mixture Tool; the issue associated with the screening model plumes should be gone.


Microsoft Excel - Book4
File Edit View Insert Format Tools Data Window Help Adobe PDF
Spelling... F7
Research... Alt+Click
Error Checking...
Speech
Shared Workspace...
Share Workbook...
Track Changes
Euro Conversion...
Compare and Merge Workbooks...
Protection
Online Collaboration
Solver...
Goal Seek...
Scenarios...
Formula Auditing
Macro
Add-Ins...
AutoCorrect Options...
Customize...
A1


Microsoft Excel - Book4
File Edit View Insert Format Tools Data Window Help Adobe PDF
Favorites Go Book4
A1
Add-Ins
Add-Ins available:
Analysis ToolPak
Analysis ToolPak - VBA
Conditional Sum Wizard
Euro Currency Tools
Gradient Contour Chart
Internet Assistant VBA
Lookup Wizard
Solver Add-in
UCL version 1.0
OK
Cancel
Browse...
Automation...
Analysis ToolPak - VBA
VBA functions for Analysis ToolPak

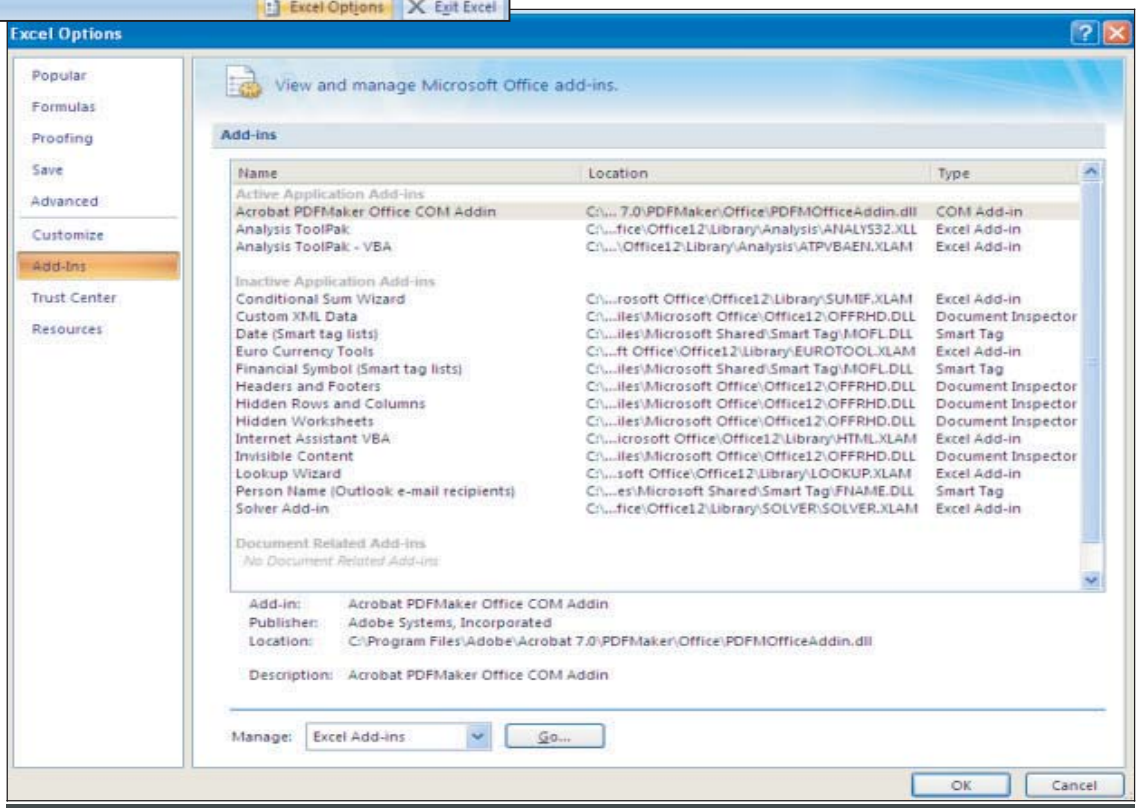
Excel 2007:

Using the Office button (pictured to left) will show the following:

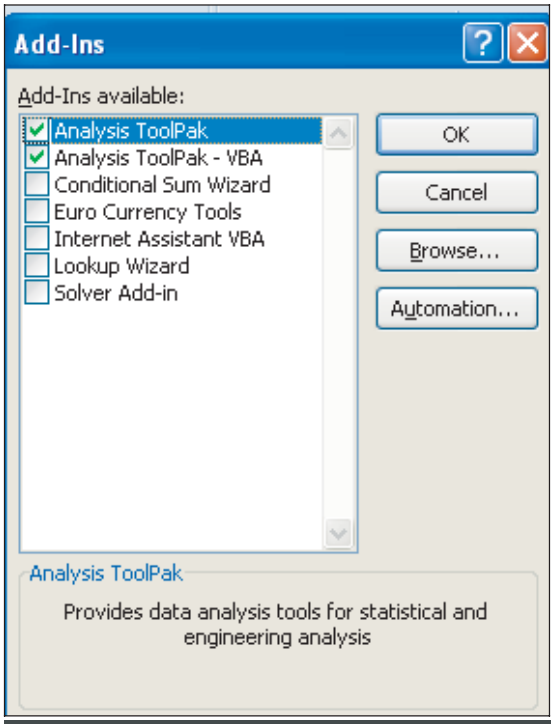


Here, the user will select the highlighted button at the bottom (Excel Options) which will allow access to a number of application-wide settings.

Once the "Options" window is open, select the "Add-Ins" tab on the right. This will display a window which looks like the image below. Select the "Go" button at the bottom of this window.



The following menu will open. Simply check the boxes next to "Analysis ToolPak" and "Analysis ToolPak – VBA," then select "OK." Close Excel and reopen it; then run the Chemical Mixture Tool, and the issue associated with the screening model plumes should be gone.



5.3. Spreadsheet-Related Problems

The Tool was built in the Excel spreadsheet environment and spreadsheet-related problems may occur for either the cell/table format or the component plume due to the calculation process. Below are some anticipated problems and interpretations:

1) #### is displayed in a number box in the Output Table: The cell format is not compatible with the value, (e.g., the number is too big to fit into the window). To fix this, select the cell, pull down the format menu, select "Cells" and click on the "Number" tab. Change the format of the cell until the value is visible. If the values still cannot be read, select the format menu, select "Cells," and click on the "Font" tab. Reduce the font size until the value can be read.

2) #DIV/0! is displayed in the raw data for the screening model plume: The raw data for the screening model is located in the bottom of the screening model interface. The most common cause of this problem is that some input data in the screening model are missing. In some cases, entering a zero in a box will cause this problem. Doublecheck to make certain that all of the input cells required for your run have data. In addition, as described in 5.2, the ERROR Function required for the Screening Model may cause this issue (Please see the troubleshooting section 5.1 for detailed assistance).

3) The plume graphs seem to move around or change size: The screening model plume is generated by Excel Standard Chart Wizard. This is a feature of Excel. When graph scales are altered to accommodate different plotted data, the physical size of the graphs will change slightly, sometimes resulting in a graph that spreads out over the fixed axis legends. The research team has adjusted the graph scale (i.e., axis scale and the plume display contours) according to the plume sizes. However, users still can manually resize the graph to make it look nice again by double-clicking on the graph and resizing it (refer to the Excel User's Manual).

5.4. General

Most unexpected, abnormal behavior can be resolved by:

- Restarting Excel,
- Rebooting your computer, or
- Returning to the original zipped document and re-extracting a fresh copy of the tool.

This tool's main limitation is that it cannot be used for all chemical substances, with the database of 740 components derived from literary research and interviews with professional personnel based on hazardous material classification and commodity flow survey and incident reports. The intended application domain is for liquid organic chemicals, particularly petroleum and related compounds. Inorganic and organometallic chemicals generally are outside the tool's domain. If the desired chemical is out of the tool database, the current tool will not be able to generate the property for the particular mixture and simulate the fate and transport in subsurface.

Detailed information concerning the development, performance, and application of the tool, as well as the individual programs (e.g., Universal Functional Activity Coefficient (UNIFAC) model, Raoult's Law, and the Cosolvency-Log K_{ow} Model) contained within it, can be found within the theoretical section of the tool development manual. If there are any issues that are not resolved by the manual, please contact HSA Engineers & Scientists at (239) 936-0789 or **hsa-ftm@hsa-env.com**.

LIST OF ACRONYMS AND SYMBOLS

AAR	Association of American Railroads
API	American Petroleum Institute
ATSDR	Agency for Toxic Substances & Disease Registry
BTEX	benzene, toluene, ethylbenzene, and xylene
BTS	Bureau of Transportation Statistics
CAMEO	Computer-Aided Management of Emergency Operations
CAS #	Chemical Abstract Service registry number, which is unique identification for chemicals. It is also referred to as CAS RN.
CFS	Commodity Flow Survey
CHEMTREC	Chemical Transportation Emergency Center
DGAC	Dangerous Goods Advisory Council
DNAPL	Dense Non-aqueous Phase Liquid
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
EAWAG	Swiss Federal Institute for Environmental Science and Technology
EPA	U.S. Environmental Protection Agency
EPIWIN	Estimation Program Interface Suite
FDEP	Florida Department of Environmental Protection
FGCU	Florida Gulf Coast University
HAZMAT	Hazardous Materials
HMCRP	Hazardous Materials Cooperative Research Program
HSDB	Hazardous Substance Data Bank
HSSM	Hydrocarbon spill screening model
IAFC	International Association of Fire Chiefs
IRIS	Integrated Risk Information System
ISI	Institute for Scientific Information
IUPAC	International Union of Pure and Applied Chemistry
KOPT	Kinematic Oily Pollutant Transport
LFER	Linear Free Energy Relationship
LNAPL	Light non-aqueous phase liquids
LSER	Linear Solvation Energy Relationship
LSST	Linear Solvation Strength Theory
MHMI	Managing Hazardous Materials Incident
MIT	Massachusetts Institute of Technology
MOFAT	Multiphase Flow & Multicomponent Transport Model
MSDS	Material Safety Data Sheets
NAPL	Non-aqueous Phase Liquid

NIST	National Institute of Standards and Technology
NOS	Not Otherwise Specified
NTSB	National Transportation Safety Board
OPP	Office of Pesticide Programs
TRB	Transportation Research Board
TSG	Transient Source Gaussian Plume
UN/NA #	United Nations or North American Identification Numbers
Aerobic $t_{1/2}$	The half-life time of a component under aerobic conditions. The smaller the half-life time, the faster the chemical decay.
Anaerobic $t_{1/2}$	The half life time of a component under anaerobic conditions
D_a	Diffusion coefficient in air
D_w	Diffusion coefficient in water
D_m	Diffusion coefficient in mixture
f_{oc}	Fraction organic carbon
I	Hydraulic gradient (ft/ft)
K	Hydraulic conductivity (ft/yr)
$K_{i, am}$	Partition coefficient between air and the mixture, which is relevant for phase equilibrium and the concentration in air
$K_{i, aw}$	Partition coefficient between air and water (unitless)
$K_{i, mw}$	Partition coefficient between the mixture and water, which is relevant for phase equilibrium and the solubility in water
$K_{i, oc}$	Partition coefficient of a component between organic carbon and water, which is relevant for adsorption of a NAPL to sediment and the retardation factor of a NAPL travel velocity
K_{ow}	Partition coefficient between octanol and water
MW	Molecular weight of the component, which is unique for each chemical
ρ	Density
σ	Surface tension of a NAPL against air
σ_{ow}	The interfacial tension between the mixture and water
P	Vapor Pressure
S	The solubility in water
η	Dynamic viscosity
$\sigma_{i,j}$	As the co-solvency power of the solvent for the compound i in co-solvent j
γ	Activity Coefficient
C_s	Concentration in Source Zone (mg/L)
C_0	Concentration in Source Zone at t=0 (mg/L)
α_x	Longitudinal groundwater dispersivity (ft)
α_y	Transverse groundwater dispersivity (ft)
α_z	Vertical groundwater dispersivity (ft)
λ	First-order decay coefficient for dissolved contaminants (yr^{-1})
k_s	First-order decay term for source concentration (yr^{-1}) (no decay for the source concentration based on the assumption of continuous source plume)
θ_e	Effective soil porosity
θ–	Soil total porosity
R	Constituent retardation factor

Abbreviations and acronyms used without definitions in TRB publications:

AAAE	American Association of Airport Executives
AASHO	American Association of State Highway Officials
AASHTO	American Association of State Highway and Transportation Officials
ACI–NA	Airports Council International–North America
ACRP	Airport Cooperative Research Program
ADA	Americans with Disabilities Act
APTA	American Public Transportation Association
ASCE	American Society of Civil Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATA	Air Transport Association
ATA	American Trucking Associations
CTAA	Community Transportation Association of America
CTBSSP	Commercial Truck and Bus Safety Synthesis Program
DHS	Department of Homeland Security
DOE	Department of Energy
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FHWA	Federal Highway Administration
FMCSA	Federal Motor Carrier Safety Administration
FRA	Federal Railroad Administration
FTA	Federal Transit Administration
HMCRP	Hazardous Materials Cooperative Research Program
IEEE	Institute of Electrical and Electronics Engineers
ISTEA	Intermodal Surface Transportation Efficiency Act of 1991
ITE	Institute of Transportation Engineers
NASA	National Aeronautics and Space Administration
NASAO	National Association of State Aviation Officials
NCFRP	National Cooperative Freight Research Program
NCHRP	National Cooperative Highway Research Program
NHTSA	National Highway Traffic Safety Administration
NTSB	National Transportation Safety Board
PHMSA	Pipeline and Hazardous Materials Safety Administration
RITA	Research and Innovative Technology Administration
SAE	Society of Automotive Engineers
SAFETEA-LU	Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (2005)
TCRP	Transit Cooperative Research Program
TEA-21	Transportation Equity Act for the 21st Century (1998)
TRB	Transportation Research Board
TSA	Transportation Security Administration
U.S.DOT	United States Department of Transportation