# Section 6.0 **EXAMPLE PROBLEMS**

This section provides example problems to assist the user in understanding the use of the LNAPL partitioning and transport screening tool. The interpretive value of the evaluations depends on understanding the principles provided in prior sections, and the constraining assumptions of the calculation methods. Therefore, the primary focus is to *show the application of the principles* to site conceptual models. The importance of good hydrogeologic judgement in selecting parameter values and understanding the impact of their uncertainty has already been discussed. This screening model is intended to reflect general principles and processes, not highly detailed site specifics. You certainly can and should "dial" in parameter ranges using site specific observations, but attempts at highly detailed calibration are unlikely to better the results. You can get the big pieces right and still expect to have nuances that fall outside the range of the conditions considered. Piecing together and interpreting the results is the key to success.

In this evaluation process, one typically brackets site hydrogeologic and LNAPL conditions as they may pertain to specific regulatory, business, or public concerns. The facets of the evaluations applicable to those issues may encompass only a portion of the calculation output. For instance, if one were interested in the potential longevity of a chemical compound in fuel in a permeable horizon, one may use properties that represent that specific geologic horizon, but not surrounding materials. Thus, the results from the calculations would not be used directly to infer broader site conditions, but would rather be placed in context as one portion of overall conditions.

The first problems of this section are primarily tutorial, although they also give framework for thinking through the calculation process. The last problem is from a more complicated site to provide some insight into possible interpretive scenarios that might be developed. The permutations possible in the calculations are too extensive for complete treatment. The user will need to forge forward based on the understanding of the underlying physics, hydraulics, chemistry, and transport principles.

# 6.1 PROBLEM #1: TUTORIAL EXAMPLE

This first problem is highly simplified and has no site specific interpretive goals. The problem is setup for a homogenous fine-sand condition, with an equilibrium distribution of LNAPL in the source zone at an observed well thickness of 1 m (~3.3-ft). This baseline condition will be compared to the condition at the end of 3 years of simple LNAPL skimming. Example values for each property data set are used throughout most of this problem, with a few exceptions to show how user-defined inputs are added. The fuel for this example is gasoline without MTBE or other oxygenated compounds. The various parameters and operation of the program will be highlighted by API-LNAST screens, and it is suggested that you have the software running while you go through the problems.

A problem is started by opening the API-LNAST program. When the program is executed, an introduction screen showing the version and compilation data appears (Figure 6-1). Select the **OK** button, and the program will open the main screen, where the various properties tabs will show up (Figure 6-2). This example problem will proceed sequentially through

API LNAPL Source Depletion Screening Tool
API-LNAST
LNAPL Dissolution and Transport Screening Tool
Version 1.50
Written by David Huntley and G.D. Beckett
For the American Petroleum Institute
November 1, 2000
ОК

Figure 6-1, LNAST introduction screen. Select **OK** to start a problem.

Calculate view Dut	Problem [	Description: Tutorial P	roblem #1	
Soil Properties	Groundwater Conditions	Source Area Parameters	LNAPL Properties	Solute Transport Properties
Conditions	C Vertically Lay Conditions	ered	<b>Soil Type</b> Fine Sand (K= 1 m/day)	¥
			Van Genuchten Alpha (1/m)	7.5
			Van Genuchten n	1.9
Saturated Hydraulic Conductivity (m/day)	1		Residual Saturation of Water	0.15
Total Porosity	0.4		Field Residual Saturation of LNAPL	0.14
			OK	Cancel Changes

Figure 6-2. **Soil Properties** Tab for example Problem 1. A fine-sand has been selected from the **Soil Type Box**, and the example parameters are automatically provided.

the parameter screens from left to right. There is, however, no need to start with any one properties tab, but doing things in a systematic way typically decreases mistakes or confusion as analyses progress. The top menu line above the parameter input screens is used after the input selections are made, as discussed below.

First select the **Soil Properties** Tab. In that tab, there are several parameter requirements, as discussed in Section 5. For the purposes of learning, the **Homogeneous** conditions button will be selected. Later on in the problem sets, the layered heterogeneity condition will be used. Under the **Soil Type** drop box, select the fine-sand (Figure 6-2). Example parameters for this type of material will be placed in each entry box on the page, with a last reminder that the example parameters come from a variety of sources and may not apply to your particular site problem. You can replace any parameter with a site specific value by highlighting the input box with your cursor, and typing in the updated value. Remember that all data units must be consistent with those requested by the utility. For this page, length units are meters and time is in days. You may place a problem name and description in the Text Box that is present on the upper right of the utility frame.

The next Tab in the software utility (**Groundwater Conditions**; Figure 6-3) is for specifying regional groundwater flow conditions. Simply input the regional gradient, the regional specific discharge, or the average pore velocity. Each of these are related through Darcy's Law (Appendix B). Be aware that when one selects a layered condition, the only option is to input the regional groundwater gradient because the conductivity of each layer will be different and a uniform groundwater flow specification will not apply. For this example problem, we will input a hydraulic gradient of 0.005. Click the gradient selection button, highlight the input box, and type in the gradient value.

The Source Area Parameters Tab is selected next. As discussed previously, this Tab controls the geometry and physical distribution of the LNAPL source in the water table region. As noted above, this calculation will compare equilibrated LNAPL conditions for the default example thickness (1 m) to the ending conditions after 3 years of product skim-



Figure 6-3. The hydraulic gradient options in the Groundwater Conditions Tab.

Problem Description:	Tutorial Problem	1#1	
Soil Properties Groundwater Conditions Param	Area L	NAPL Properties	Solute Transport Properties
ethod Used to Calculate LNAPL Saturation C Equilibrium LNAPL Distribution Distribution after Fixed Period of Remediation Distribution at Minimal Mobility Residual Saturation User Input of Distribution Edit Saturation Distribution Distribut	Cancel Changes	Source Area I Initial Thickness of LNAPL (m) Average Depth I top of LNAPL (m) Length of LNAPL Zone (m) Width of LNAPL Zone (m)	Geometry 1 10 10 10 5 5

Figure 6-4. The Source Area Parameters Tab with the example selections for the first part of Problem #1. The LNAPL distribution is at vertical equilibrium, and the geometry as given on the right.

ming. Each problem for the comparison is run separately (VEQ versus skimming). So, for now, allow all example defaults on this page to remain unchanged (Figure 6-4). After the first problem has been executed, which will happen after we input the remaining information, we will come back to this page and change the source area description by adding skimming.

The next Tab in the utility is the LNAPL Properties selection. We will leave all values as given in

the example screen for gasoline, except that we will remove MTBE from consideration, as the problem applies to gasoline without oxygenated additives. To remove MTBE from consideration, click on the "Remove Constituent" button on the bottom of the page. This action will bring up a selection box that provides the compound list under consideration. Highlight MTBE with the cursor, and a confirmation box will appear asking if the compound is really to be deleted (yes/no; Figure 6-5). Select "Yes", and MTBE will be removed from the table of compounds under consideration. The list of remaining com-



Figure 6-5. Remove MTBE by highlighting the compound in the Remove Constituent list, and confirm the deletion by selecting **Yes** in the confirmation box.



Figure 6-6. Solute Transport Properties Tab with the selected parameters for Problem #1.

pounds includes benzene, toluene, ethyl benzene, and xylene. The remaining LNAPL properties will stay unchanged for this example (Figure 6-4).

The last Tab in the LNAST utility is the Solute Transport Properties section where the groundwater and transport factors are input. We will use the example values in all fields for this tutorial problem (Figure 6-6). Notice that there is an option at the lower left for time stepping sensitivity. Fewer time steps result in shorter calculation times, but may loose some desired refinements. Typically, fuels with highly soluble compounds, like MTBE, alcohols, or other additives are more likely to benefit from time stepping refinements because the rate of mass loss of these compounds will be high relative to other low solubility species. The resulting contrast in the mass loss rates between compound can cause spiky output with fewer time steps.

The properties necessary to run a problem have now been fully specified, and the calculations can be performed. As noted in the User's Guide (Section 5), a calculation proceeds in the following step-wise manner. If remediation is considered as the specification for the LNAPL distribution, that must be run before other calculations (as discussed below in the second half of our example problem). Next, the depletion of soluble and volatile components from the LNAPL is calculated to determine the time dependent concentrations in the groundwater phase in the source zone. Last, the groundwater transport of the selected compounds of interest are calculated based on the output from the first calculation. In the case of a remediation measure, as in the second part of this problem, one must first perform the remediation estimate to determine the LNAPL conditions for the partitioning calculations. So for this first part, we will select Calculate from the top menu, and then select the Include Volatilization option (Figure 6-7).

The LNAST utility will calculate the depletion of the specific compounds of interest and display a table of results. One may **Graph** and/or **Save** the results by selecting either option on output table screen (Figure 6-8). Because we are performing a comparison problem, we will save the information to a tab-delimited file that we can later graph in a spreadsheet. Name the file with an extension that you will remember, for instance \*.DEP signifying a depletion data file. We will save and name the output "PROB1A.DEP".

Calculate View Output Help		
LNAPL Recovery		roblem Description: Tutorial Problem
LNAPL Source Depletion	•	Include Volatilization from Source
Downgradient Dissolved Phase	• •	Exclude Volatilization from Source

If you wish, you can also View, Save and/or Graph the LNAPL distribution estimated for the properties that have been selected. To do so, go to the View menu at the top of

Figure 6-7. From the **Calculate** pull-down menu, select the **LNAPL Source Depletion** option, and then the **Include Volatilization from Source** sub-option.

the main program and select the **Hydrocarbon Saturation Distribution** option. When selected, this will show a table of the LNAPL distribution associated with the problem. This can be graphed or saved. Again, the Save option will be selected so that these conditions can be compared to the second half of the problem (save as PROB1A.SAT).

We are now ready for the second part of this first set of calculations. Again pull down the **Calculate** menu with the cursor, and this time select the **Downgradient Extent** option. There are 2 suboptions, one for the downgradient extent of the compounds of interest at the selected target concentrations, the second for calculating the time-concentration profile at user specified distances. For this comparative calculation, we will select the downgradient extent. A timer bar appears at the bottom of the

а,	Source Are	a Dissolved	l Phase Cor	ncentration	s (mg/l)	
Sa	ive as File – G	iraph				
			1	nitial LNAPL I	Mass = 504	4 kg
			Concent	ration in	i mg/l	
	Time (yrs)	Benzene	Ethyl Benzei	Toluene	Xylene	<b></b>
	0.e+0	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	2.74e-7	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	6.02e-7	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	9.97e-7	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	1.47e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	2.04e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	2.72e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	3.54e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	4.52e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	5.69e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	7.11e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	
	8.8e-6	3.2e+1	2.43e+0	4.07e+1	1.31e+1	

Figure 6-8. This output table is provided once the source area depletion calculation is complete. One may **Save** and/or **Graph** the output.

screen while the calculation executes. This will take a few seconds to a few minutes depending on several factors including the number of compounds selected, the time stepping refinement, and your computer processor speed. Once the calculation is complete, a results table again appears with the same options as the last (graph and/or save). Because we will make a comparison between this result and that following simplified skimming, we will also save this file now as "PROB1A.DXT", with the DXT extension indicating that this is the downgradient extent output file. Again, all files are stored as tab-delimited text. This would also be a good time to save the problem file itself by pulling down the File, Save option from the main pull-down menu at the top of the utility. This file is automatically saved with the extension "API" (PROB1A.API). This input file can be opened anytime to run a comparison against any other set of conditions.

The second half of this comparison problem can now be executed. Because all factors are the same except the change of LNAPL distribution to a post-skimming condition, all that is needed to rerun the problem is to go back to the **Source Area Parameters** Tab and select the Distribution after a Fixed Period of Remediation option (Figure 6-9). Now when the calculate menu is pulled down, notice that the first allowable calculation is



Figure 6-9. Calculate LNAPL recovery after resetting the Source Area Parameters to the Remediation option.

for the remediation condition, because this is needed to describe the LNAPL distribution on which dissolution will act. Note that because the old problem is still in memory, jumping to the Downgradient Dissolved-Phase calculation would merely reproduce the prior result, and not the new result after skimming. Be sure to always proceed through the calculations in the correct order, which follows the listing from top to bottom in the Calculation menu options as discussed previously.

Once the LNAPL Recovery option is selected, a new screen will appear that contains all the input specifications needed for the problem (Figure 6-10). First select the Skimmer Well button. The software will then highlight the input boxes that require parameters. We will leave the inputs at the default example settings. Recall that a more thorough definition of the inputs and requirements is provided in the User's Guide (Section 5), and in Appendix A that documents the remediation approximations by Charbeneau et al., 1999. The remediation estimate is run by selecting the **Calculate Recovery** button on the right, under the Input Values table. The output table will be filled with the results, which will remain stored in memory for the remaining two portions of the calculation (depletion & transport). As with all other output, you may save and/or graph the results by selecting those options at the top of the menu.

As mentioned, the next stage is to calculate the depletion of the selected compounds from the LNAPL source zone that remains after the skimming effort. The depletion calculation is done in the same way as before. Simply select the **Calculate** pull down menu, and **LNAPL Source Depletion** option, with the **Include Volatilization** sub-option. This will produce a table analogous to the first half of this tutorial problem, that may again be graphed and/or saved. Because we are making a



Figure 6-10. The remediation calculation screen with Skimmer Well selected, along with the inputs on the right that define the skimmer well operations.

comparison, we will save the output as "PROB1B.DEP" for later graphing in a spreadsheet. The LNAPL saturation distribution will also be saved from the View menu (PROB1B.SAT). Now the **Downgradient Extent** calculation may be run, again, exactly as in the first half of the problem. **Save** the output file as "PROB1B.DXT".

Both halves of this simple tutorial problem are now complete. The key results will be graphed comparatively, as mentioned, using a spreadsheet program. Any graphing software may be used to construct these comparative charts. Alternatively, one could also just print key results from within the software routine for each calculation and visually compare the graphical results. The key is that the LNAST utility can only graph one set of calculations at a time. If is often more illustrative to combine different calculations into a single graph, as will be done here for explanatory purposes. Each of the output files can be brought into the graphing routine you have selected as a tab-delimited file. Three sets of output files have been saved; 1) Saturation (\*.SAT); 2) Source depletion (\*.DEP); 3) Downgradient extent (\*.DXT). Each will be compared in order.

The LNAPL saturation distribution for each part of the problem, as discussed extensively in prior sections, controls the mass distribution and flux of chemicals from the source area. It is of interest then to compare the difference between the "ambient" condition of vertical equilibrium of the LNAPL to the condition after 3 years of skimming recovery (Figure 6-11). As seen, the profiles are similar for areas where the LNAPL saturation is below residual. The remainder of the ambient profile is the theoretically recoverable LNAPL. Recall again that these recovery approximations are usually optimistic compared to field conditions.



Figure 6-11. LNAPL saturation profiles for ambient and post-skimming conditions. The "nub" in the skimming profile is the remaining theoretically recoverable LNAPL.



Figure 6-12. Water relative permeability under ambient and skimming conditions. Notice that skimming increased the relative permeability to water by removing LNAPL.

It is also of interest to inspect how the depletion of LNAPL from skimming changed the relative permeability with respect to groundwater that is flowing through and below the zone of LNAPL impacts (given in the output file). As expected, the relative permeability to water increased due to removal of LNAPL (Figure 6-12). In turn, we might expect some degree of faster partitioning of compounds to the water phase as the flux through the LNAPL has increased accordingly. This comparison is given below.

Next, the depletion of benzene and xylene is contrasted between the two problem halves, as well as contrasting compound specific outcomes. As seen, the "residence" time of benzene is suggested to be depleted by a little more than half, from about 90 years to 40. It is also clear that less soluble and volatile compounds, like xylene, will remain for significantly longer periods. The reason for the depletion gain is that, for this particular example, there was a significant

recoverable fraction estimated from the LNAPL source zone (from about 5,000 kg to 2,100 kg in the source zone).



Figure 6-13. Comparison of chemical depletion from the source area for benzene and xylene.



Figure 6-14. Estimated downgradient extent of benzene and xylene for each of the two LNAPL source conditions.

Last, the downgradient extent conditions can be compared for the same compounds and conditions (6-14). Recall that this calculation is based on the target concentration specified in the LNAPL Properties Tab. Therefore, the extent is a plot of the downstream migration at that particular concentration. It does not mean that detectable concentrations are not present beyond that distance, but simply that those detections would not be estimated to be above the selected target threshold. This is the primary reason, though not the only, that the downgradient extent of xylene is much smaller than benzene (about 0.3 versus 16 m, respectively). Notice also that the total downgradient extent is not affected by remediation for this case because the time of spreading downstream is much smaller than the depletion time of compounds of concern.

This example problem provides the

tutorial background necessary to run the software. However, only simple interpretative evaluations were included as part of the problem. The next tutorial problem is relatively simple also, but is taken from our site database. A bit more time will be spent on the conceptualization of the problem, and interpretive aspects.

## 6.2 PROBLEM #2: GASOLINE IN A COASTAL DUNE SAND, AMBIENT EVALUATION

This problem is a relatively simple condition patterned in a general way after a real site, though the purpose here is not to go into site specifics, but rather to explain the concept of site bracketing. This problem extends the tutorial problem by showing how interpretations of soil parameter values can be used to extend and compare results. The problem will also show how using some interpretive common sense is necessary to producing meaningful results.

The site subsurface consists of coastal dune sands that are composed of uniform fine-grained sand, with a hydraulic conductivity of about 3 m/day. The water table is relatively stable about 10 m below grade with a gradient of 0.003 m/m. The LNAPL source is assumed to be gasoline without MTBE, and has been observed at thicknesses of 1.25 m in several wells within the heart of the source zone, with plume width and length averaging 10 m in the zone of significant product accumulations. For the actual site, we know the measured capillarity, but will assume that we do not so that we can show how one might go about a bracketing a screening estimate.

## 6.2.1 Defining the Problem

The dune sand condition suggests that we have a homogeneous geologic environment, so we will select that calculation option (i.e., no layering). We have been given hydraulic conductivity, but do not know any other geologic or fluid parameters. The K value given is between the fine- and medium-sand default values in LNAST, so we can compare the outcomes between the remaining properties associated with each of those example soils, plus one site specific soil estimate (key values, Table 6.1). So, although this is a homogeneous setting, we will need to bracket a range of possible soil conditions to gain insight into the problem and examine the which parameters appear most representative. We will use the default example soil parameters (except K, which was given) for the fine- and medium-sand selections, and compare with a site specific soil parameter estimate.

For this particular problem, the capillary properties are the most important unknown. For the site specific soil, one might suspect that the pore distribution of a very well sorted sand will be uniform, corresponding to a larger sorting index of approximately 4.5 (Van Genuchten n parameter). Recall that higher n values suggest more uniform pore sizing and grain sorting. Taking the grain-diameter associated with fine-sand, one also could estimate that the capillary rise parameter could be as small as 1.5/m. Three soil types are now described (Table 6-1) that will be used for each calculation set. Recall that these are placed into the calculation set through the **Soil Properties** Tab.

The hydraulic gradient was given, so we will use that input in the **Groundwater Conditions** Tab (not pictured). In the **Source Area** Tab (Figure 6-16), we will input the source geometry information provided and select Equilibrium LNAPL Distribution. We will assume the 1.25 m thickness

<b>8</b> , I	NAPL Dissolution an	d Dissolved Phase Tra	nsport		
File	Calculate View Out	put Help			
		Problem D	escription: Tutorial Pr	oblem # 2; Dune Sand w	/Gasoline
ſ	Soil Properties	Groundwater Conditions	Source Area Parameters	LNAPL Properties	Solute Transpo Properties
	<ul> <li>Homogeneous Conditions</li> </ul>	C Vertically Laye Conditions	ered	<b>Soil Type</b>  Fine Sand (K=1 m/day)	<u> </u>
				Van Genuchten Alpha (1/m)	7.5
				Van Genuchten n	1.9
	Saturated Hydraulic Conductivity (m/day)	3		Residual Saturation of Water	0.15
	Total Porosity	0.4		Field Residual Saturation of LNAPL	0.14

Figure 6-15. Soil Properties Tab showing a set of conditions for Case 1.

condition as given, and a plume width and length equal to 10 m. Finally, moving to the **LNAPL Properties** Tab (Figure 6-17), we will choose the default gasoline selection, but since there is no MTBE in the fuel, we use the **Remove Constituent Option** and remove MTBE as a constituent of concern. For instructional purposes, we will leave the remaining compounds. However, the realworld problem would be primarily concerned with benzene, as other COCs present a much smaller relative risk.

For comparison purposes, we will contrast the VEQ conditions for the 3 soils with a prescribed minimum LNAPL mobility condition equal to  $8.64 \times 10^{-4}$  m/day (1 x 10<sup>-6</sup> cm/sec). This problem then will result in a comparison of 2 primary conditions, each with 3 different soil conditions (Table 6-1), for a total of 6 calculation sets.

# 6.2.2 Running the Problem

We have the 3 sets of soil inputs described above (Table 6-1) that will be run for VEQ (odd numbered cases) and minimum mobility conditions (even numbered cases). The program allows projects inputs to be saved to disk. Since all but a few parameters will remain unchanged for each calculation, it is suggested that a base project be saved that can then be updated for each additional run by systematically changing just the new parameters. Each run can then be saved as new project file, so a permanent record will exist for the full problem set.

Soil Parameters		Cases	
	1 & 2 fine-sand	3 & 4 medium-sand	5 & 6 site sand
Hydraulic Conductivity (m/d)	3	3	3
Porosity	0.4	0.4	0.4
Effective Porosity	0.34	0.364	0.34
VG alpha	7.5	14.5	1.5
VG n	1.9	2.7	4.5
Residual water saturation	0.15	0.09	0.15
Specific Oil Retention	0.14	0.12	0.14

# TABLE 6-1SOIL PROPERTIES FOR PROBLEM #2

Before executing any new run, make sure your new inputs are correct. When you type a value in an input box, hit enter or move the cursor after the entry. The **Cancel** button will reset values to the example parameter set up until the time that the **OK** button is hit. We will start with the fine-sand VEQ condition (Case 1) as our example, the remainder of the problem sets will not be explicitly discussed as the necessary changes are straightforward. Going to the Soil Properties Tab, we will select the fine-sand default parameters, with the exception of the hydraulic conductivity, which was given as 3 m/d (Figure 6-15). Next, we will input the given hydraulic gradient (0.003) in the Groundwater Conditions Tab (not shown). Now moving to the Source Area Parameters Tab, we select Equilibrium LNAPL Distribution as the method to calculate LNAPL saturation VEQ conditions and input the given plume geometry information (Figure 6-16). As discussed so long ago, one should generally not use averages in the plume geometry specifications because the zones of greatest LNAPL pool thickness and saturation control the risk outcomes. Said another way, given two otherwise identical plumes with respect to total mass and area of impact, the plume having areas of more concentrated mass will present the greater risk residence time. Moving on to the last Tab, **LNAPL Properties**, we will accept all default values for gasoline except that MTBE will be removed as a constituent for consideration (Figure 6-17).

💐 LNAPL Dissolution and Dissolved Phase Transport		<u>_</u>
File Calculate View Output Help		
Problem Description: Tutorial Problem # 2; 1	Dune Sand w/Gasolin	e
Soil Properties Groundwater Conditions Parameters LNAPL	Properties So	olute Transp Properties
Method Used to Calculate LNAPL Saturation	-Source Area Geo	metry
Equilibrium LNAPL Distribution	Initial Thickness	1.25
<ul> <li>Distribution after Fixed Period of Remediation</li> </ul>	Average Depth to [ top of LNAPL (m)	10.0
O Distribution at Minimal Mobility	Length of	10.0
Residual Saturation	LNAPL Zone (m)	10.0
C User Input of Distribution Edit Saturation Distribution	Width of LNAPL	10
Criteria for Minimal Mobility 1.0e-02 m/day (Hydraulic Conductivity)		
OK Cancel Changes		

Figure 6-16. **Source Area Parameters** Tab for Problem #2 showing the LNAPL geometry conditions for Cases 1, 3, and 5. For Cases 2, 4, and 6, the Distribution at Minimal Mobility would be checked, with all other parameters remaining the same.

At this point, the problem is ready to run. Before doing so, save the project by selecting the File, Save Project option in the menu at the top of the LNAST utility screen (this menu is always available above the data entry tabs) and save the project to a file name of your choice. Now select the **Calculate** menu and then select LNAPL Source Depletion (note that this is the only option available at this juncture). Two options can be selected, source depletion with or without volatilization. Since this product is gasoline and there are no geologic conditions noted that would impede volatilization, it is appropriate to select the Include Volatilization From the Source option. Once selected, the program calculates the initial saturation profile and mass throughout the LNAPL impacted interval. Then mass is depleted by water transport through the LNAPL and vapor transport above the LNAPL. Once this calculation is done, a table of time versus water-phase concentration is produced; the table also provides the integrated mass of the simple geometric plume. Remember that because the calculation assumptions are directed toward conservative aspects of the problem, this mass is a "conservative type area mass" and not the total LNAPL mass present in the subsurface, as discussed previously. Methods of better estimating the LNAPL plume mass are based on the same principles provided here, but require a bit more work. First, one must estimate the volume per unit area about each observation location containing LNAPL (gals/ft<sup>2</sup>, liter/m<sup>2</sup>, etc.) and then integrate those results across the total area of the plume. One should also include oil stranding and entrapment effects from water level variations and heterogeneity effects, as discussed previously. In the case of our problem,

NAPL Dissolution a	nd Dissolved Ph	iase Transport				
Calculate View O	utput Help Pi	oblem Descrip	otion: Tutorial F	roblem #2; [	Dune Sand w/Gas	oline
Soil Properties	Groundwater Co	onditions Sourc	e Area Parameters	LNAPL	Properties	Solute Transport Properties
CINAPL Phase Pr Hydrocarbon Ty Gasoline	operties	Density (	gm/cc) 0.73	0	lil/Water Interfacia (dynes/crr lil/Air Interfacial Te (dynes/cm) Viscosity (c	al Tension 52 n) ension 24 P) 0.62
	Pure Phase Solubility (mg/l)	Pure Phase Vapor Conc. (mg/l)	Mole Fraction of LNAPL	Log(Koc)	Biodegradation Half-Life (days)	Target Concentration (ug/l)
Benzene	1780	324	0.018	2	90	5
Ethyl Benzene	135	57	0.018	3	65	700
Toluene	515	111	0.079	2.06	60	1000
Xylene	175	38	0.075	2.6	150	10000
	Ac	ld Dissolved Constituent	Remove Constitue	e nt	ок с	Cancel Changes

Figure 6-17. Screen showing the LNAPL properties selected for Problem 2.

we have used the worst-case thickness of 1.25 m across the areal domain for each of the soil and LNAPL saturation conditions, which should produce an overestimate of the volume in-place for each calculation condition, and thus result in worst-case plume longevity conditions.

The mass depletion results just calculated are stored in computer memory as automatic input into the groundwater contaminant transport calculations by the Domenico approximation (1987, 1990). Two options are available in the **Calculate** menu to make the next step in the process. One may ask the program to calculate the downgradient extent of dissolved compounds of interest based on the user selected target concentration, or the program can also calculate the time dependent concentration at individual locations directly downgradient of the LNAPL source along the center of axis. The results of these latter calculations are often termed "breakthrough curves". We will use both options for our analysis of the results, first running the downgradient extent, and then calculating breakthrough curves at 5, 10, and 30 m downgradient.

## 6.2.3 Results

The most significant observation regarding this set of evaluations is the large difference created because of the range of soil capillary conditions that were estimated. Particularly, the mass and impact of the best-guess dune sand parameters were much less than the default conditions for the parameters we estimated to be more representative for the specific dune sand in question. The initial mass for the cases ranged from a low of approximately 1,690 for Cases 5 & 6, to a high of about 25,700

kg for Case 3 (Figure 6-18). Obviously, the range of capillary properties selected has a significant influence on the results. Equally obvious, the Case 5 conditions did not exceed the minimum mobility threshold, and therefore were identical to Case 6. So for this site, the hydraulic conductivity was relatively high, but did not correspond to a smaller capillary rises (larger ) that would have been expected using the "ex-



Figure 6-18. Comparison of initial mass conditions for the six cases in Problem 2.



Figure 6-19. Initial LNAPL saturation profiles for the 3 soils and 2 initial conditions used for Problem #2.

ample" sands. The user should now recognize the problem with using the example parameter sets in Appendix C and the LNAST utility without site specific reasoning.

The results of this evaluation can be best understood by first reviewing each of the initial LNAPL gasoline source profiles (Figure 6-19), which as will be recalled, control both the total mass and the relative groundwater flux through the source interval (Figure 6-20). The medium sand (Cases 3 & 4) exhibits the greatest ambient saturation, and therefore smallest groundwater effective conductivity and flow through the source (Figure 6-20), the fine-sand (Cases 1 & 2) the next smallest saturation and greater groundwater flow. Our best-estimate capillary conditions (Cases 5 & 6) exhibit the least oil saturation and therefore the greatest groundwater flow through the source interval. Notice for the minimum LNAPL mobility condition, both the example fine- and medium-grained sand conditions



Figure 6-20. Relative groundwater flow through the gasoline interval. Since K is equal for all cases, the results show the important effects

(Cases 2 & 4) are truncated to meet that condition, whereas the bestestimate capillary conditions are below this threshold at ambient conditions (Figure 6-19). Among other things, this means that there would be no appreciable gain in attempting hydraulic recovery of the "best-estimate" condition (Cases 5 & 6) because the product would be at saturations below the lateral mobility threshold. At the same time, there was certainly LNAPL recovered for cases where the LNAPL saturation was greater than residual.

The source depletion of benzene from the LNAPL is highly sensitive to soil capillarity and initial conditions. However, the results are again interesting in their synergistic and non-intuitive aspects. With volatilization, the benzene source depletion for all conditions falls between about 20 and 150 years (Figure 6-21). This is at first surprising when we recall that each condition has the same regional groundwater flow rate and that soil condition #3 has significantly greater initial mass than the other conditions (Figure 6-18). For instance, the benzene depletion time for the best-guess fine-

sand parameters is about the same as the depletion time for Case #3, the medium sand. Why? Recall that we selected the source depletion with volatilization option. The integrated effective vapor diffusion rate is several times greater for the medium sand than it is for the fine sand with best-estimate capillary parameters (Figure 6-22). This shows the potential importance of volatilization for coarser grained materials. If we look at source depletion without volatilization, we see results that make more intuitive sense (Figure 6-23). Aspects of volatilization to ground surface and into build-



Figure 6-21. Benzene source depletion curves for Cases 1-6 including unimpeded volatilization from the source zone.



Figure 6-22. Vapor diffusion tortuosity factor for each soil condition based on the Millington-Quirk equation



Figure 6-23. Benzene depletion curves without volatilization. Compare times to those in Figure 6-21.

ings are important to risk assessment. The reader could benefit by reviewing documents pertaining to vapor transport (ASTM, 1995; API, 1999).

Keep in mind that the key assumptions of homogeneity, moisture equilibrium, and connectivity to ground surface results in artificially large vapor flux to ground surface. In the author's experience, vapor flux limiting zones exist at most sites, be they simple site cover conditions, high soil moisture impediments or more complicated heterogeneities. Without high volatilization rates, one would expect the oil residence time to be significantly larger for Case 3 than for Case 5 & 6 (Figure 6-23). Under these vapor limited conditions, the medium-grained poolwould be resident about 50 times longer than the best-estimate fine-grained sand. So, without belaboring the point, it is very simple to see that results are highly dependent on good judgement. If there are vapor flux limiting horizons, use the guidance given previously to determine a reasonable vapor efficiency input factor.

Last, we can look at the downgradient extent characteristics under the different soil and initial LNAPL conditions. As expected based on prior discussions, the downgradient extent of benzene (and other compounds) is essentially the same for all 6 conditions considered (Figure 6-24a). This is because the mass of LNAPL is large and depletion is slow relative to the time necessary for the plume to reach the downgradient limits and field equilibrium conditions between transport and biodecay. The plume scenarios have much different residence and contraction times due to a combination of factors, but primarily the differing volatilization aspects discussed above.

The benzene breakthrough curves (concentration versus time) 5 m downstream of the source zone show similar early time shapes and peak concentration within about a 20% range (Figure 6-24b). Again, the volatile losses and soil characteristics of the example fineand medium-grained sand soils suggest smaller peak concentrations and residence under the minimum mobility condition (Cases 2 & 4) for the reasons discussed above.

In conclusion, this example problem shows the importance of site bracketing to investigate probable soil properties controlling the LNAPL mass, distribution, partitioning characteristics, residence time and downstream impacts. The importance of the selected capillary parameters is clear, as is the potential for incorrect estimates using the example parameters derived from literature. For a site-specific evaluation, one would look to any of the specific LNAST outputs and compare to the corresponding field conditions. For instance, which breakthrough curve(s) best represent the history of groundwater monitoring results? Do the predicted LNAPL zone saturations



Figure 6-24a. Downgradient extent curves for benzene at MCL for soil and source condition.



Figure 6-24b. Breakthrough curves for benzene 5 meters from the source for each soil and source.

agree with soil sampling results or petrophysical analyses? Are the shapes and order of magnitude of the various curves consistent with field observations? The list goes on, but one can see that the purpose of the evaluations is to focus on key LNAPL aspects that control the risk related outcomes of interest.

## 6.3 PROBLEM #3: MTBE GASOLINE IN A MULTILAYER GEOLOGIC SETTING

This problem is more complex and incorporates the effects of a relatively low degradability compound (MTBE), coupled with aspects pertaining to heterogeneity and remediation by soil vapor extraction (SVE). The challenges in characterizing site conditions and the uncertainty in doing so will become evident in this example. This site, like many, has had very few of the critical parameters measured, and geologic interpretation is necessary to prescribe the evaluations. For tutorial purposes, not all the complexities of the actual site are presented here.

For this evaluation, we want to know how SVE has affected the LNAPL chemistry and conditions, and what the potential groundwater transport and residence time conditions may be for remaining impacts. For this site, the regulatory agencies and the responsible party must decide whether additional cleanup actions are needed based in part on this technical analysis.



#### 6.3.1 General Conditions

This site is a fuel service station in coastal Southern California that experienced a gasoline free product release, resulting in observable

Figure 6-25. Site plan showing well locations and historic LNAPL distribution.

LNAPL accumulations in wells historically to as much as 7-ft (Figure 6-25, Site Plan & LNAPL Plume). The problem was identified in the early 1990s during station renovation. In response to the spill, soil vapor extraction (SVE) cleanup actions were performed. After approximately 6 years of



cleanup operations, concentrations in recovered vapor (Figure 6-26) and groundwater (Figure 6-27) have decreased, and free product accumulations in wells are no longer present beyond trace levels (Figure 6-28). The initial hydrocarbon recovery rate of greater than 100 lbs/hr dropped to about 1 to 3 lbs/hr at the end of cleanup in early 1999 (Figure 6-26).

Figure 6-26. SVE recovery rate and cumulative total.



Figure 6-27a. TPH concentration in groundwater through time of SVE operations. MW-3 and MW-10 are near source zone, MW-12 is about 50-ft downgradient.



Figure 6-28. Observed free product thickness history over the period of SVE cleanup.



Figure 6-27b. Benzene concentration through time of SVE operations. MW-3 and MW-10 are near the source zone, MW-12 is about 50-ft downgradient.

Approximately 200,000 lbs of hydrocarbon have been recovered through the SVE operation. Since about half of the compounds in gasoline account for 97% of the volatility, one can estimate that roughly a similar order of magnitude mass remains of lower volatility LNAPL compounds. More important, remaining dissolved-phase groundwater impacts, and the character those impacts, suggest some of the source zone remains untreated, as discussed below.

The geologic setting is an interbedded se-

quence of sand, silty sand, and clayey horizons of predominantly marine and bay sediments. Based on aquifer testing and boring log descriptions, the sands have a hydraulic conductivity (K) of about 6 m/day, the fine-grained layers have an average K of 0.1 m/day and the contact between beds is sharp. The water table is stable about 40-ft (12.2 m) below grade with a groundwater gradient of 0.005 m/m. The stratigraphic beds have a fair degree of lateral continuity with respect to the plume dimensions in the water table region (Figure 6-29, geologic cross-section).

### 6.3.2 Defining the Problem

The layered geology indicates we should consider both the low and high permeability zones in our evaluation, using the *Vertically Layered Conditions* option on the **Soil Properties** Tab. Based on geologic logs through the LNAPL impacted interval, a 2-layer condition is a reasonable starting point, with a sandy material overlying a finer-grained bed, each 1 m thick (Figure 6-29). Hydraulic



Figure 6-29. Geologic cross-section of beds in the near area of the LNAPL release from the underground storage tanks.

### TABLE 6-2

Soil Parameters	Soil	Types
	Sand	Silty Sand
Hydraulic Conductivity (m/d)	6.0	0.1
Porosity	0.4	0.5
Effective Porosity	0.34	0.365
VG alpha (m-1)	2.5	0.6
VG "n"	2.2	1.65
Residual water saturation	0.15	0.21
Specific Oil Retention	0.15	0.20

# SOIL PARAMETERS FOR SAND AND SILTY BEDS

conductivities are known, as are capillary properties that have been measured for this formation at a nearby site (Table 6-2). The groundwater gradient is 0.005, and the remaining geologic and fluid parameters will be selected from the example parameters provided in the LNAST utility or through site related judgement.

The primary challenge and focus of this problem lies in defining the LNAPL distribution and chemistry following the SVE cleanup. SVE cleanup of free product accumulations in the water table region has many complicating factors, such as multiphase interactions and associated multicomponent chemical stripping efficiency. Efficient stripping generally depends on active vapor

flow within or just above the zone containing the gasoline. The overall thickness of the LNAPL zone of interest is can be approximated to equal the maximum product thickness observed historically (~2 m). We can feel comfortable in this initial assumption because we know that some fraction of the initial LNAPL in place must remain, both because many of the compounds have relatively low volatility and would not be efficiently removed under ambient conditions, and also because groundwater impacts are still present and emanating from an LNAPL source. We will decide on an LNAPL source distribution for our problem after thinking about the chemical impacts discussed below.

Like many sites, no detailed chemical data were collected for the SVE system nor is there any characterization of the distributed subsurface cleanup response. The only related indicator we have to work with is the decrease in the dissolved-phase groundwater impacts. At this site, decreases in source zone groundwater impacts of 1- to 2-orders of magnitude have been observed (Figures 6-27a & b) and can be attributed to the SVE operations. One can easily verify that the concentration reductions are from SVE by running LNAST with an initial condition of 7-ft of free product at hydraulic equilibrium with initial "fresh" chemical mole fractions. The results would show that natural depletion alone would be several orders of magnitude longer than the short-term observed concentration decreases that must therefore must be primarily the result of the SVE cleanup operations.

Given the significant decrease in groundwater concentrations and large mass recovery, one might naturally think that the cleanup has been successful. However, while clearly successful in some ways, nuances in the groundwater chemical data suggest cleanup has had limited effect in some zones. These cleanup limitations are the control over the remaining impacts, both in terms of magnitude and longevity of the plume. This can be understood by looking at the chemical ratios of various compounds through time. In an ideal scenario, SVE would be expected to preferentially deplete the most volatile components in the gasoline, causing a change in the overall molar fractions in the LNAPL source are resulting groundwater concentrations through time. "Light" end compounds should be more depleted than "heavier" end compounds within the gasoline hydrocarbon range. Thus, one would expect to see the volatile/soluble compounds decrease faster than those less so. This expected "ideal" outcome is not evident in the site data. Instead, while the total dissolved-phase concentrations have fallen (Figure 6-27a & b), the ratio of benzene (more volatile/soluble) to xylenes (less volatile/soluble) and other components is unchanged (Figure 6-30a & b), as is MTBE.





Figure 6-30a. Ratios of aromatic hydrocarbons in groundwater through time in MW-10. The dashed lines are the expected groundwater concentration trends under SVE stripping.

Figure 6-30b. Ratios of aromatic hydrocarbons in ground-water through time in MW-3, as in the prior figure.

This suggests that untreated LNAPL is still present in the system that is chemically similar to conditions before SVE began. But because total groundwater concentrations have fallen, something else must be happening. Because the site has varied lithologic beds, and because SVE would be expected to have limited effectiveness with depth into the aquifer because water limits vapor flow and partitioning, a working hypothesis is that groundwater dilution is now prevalent in the system. Essentially, some groundwater flow is now potentially through "clean" zones (with respect to benzene, etc.) that were formerly more impacted, and some smaller fraction of flow is through the remaining LNAPL impacted intervals containing the original chemistry. One can envision other scenarios that explain the observations, but for the sake of this tutorial, we will simply move forward with the given working hypothesis.

In prescribing the LNAPL source distribution and chemistry, we have 2 very different general approaches that produce similar but not identical results for the assumed conditions. We can use the "known" original thickness of the LNAPL zone (~ 2 m) and the "diluted" mole fractions (observed concentration/pure-phase solubility) of the compounds of concern to describe the LNAPL zone. In real terms, this would imply that the remaining high concentration zone has chemically re-equilibrated with the original LNAPL thickness interval. Or, our second choice is to assume that a discrete "layer" of LNAPL exists that is predominantly unchanged from initial conditions (using the same reasoning that created our working "model"), and we could then use a dilution factor to account for the differences in the model output and observed conditions. The dilution factor in this case is about 100 using xylenes (relatively low solubility/volatility) at MW-3 as the indicator and comparing initial concentrations to those seen after SVE remediation. This is no surprise, as this is equivalent to the approximate concentration decreases in the monitoring locations. You may also notice that the dilution factor is an approximation that does not fit all locations and compounds equally. Approximations are necessary to run screening calculations and one can make other assumptions to test against field conditions, as needed.

Of the 2 approaches to stipulating the chemistry and LNAPL distribution, the first is the simplest and is more conservative because groundwater dispersion losses are less important for a thicker LNAPL zone than for the thin discrete layer case. Also, we know that LNAPL is still present, though chemically changed, throughout the original zone of impact. Both scenarios have attributes that are representative, but neither condition represents the probable "real" conditions of heterogeneous LNAPL saturation and chemical distributions. Again, these reflect the fundamental constaints of screening evaluations. Since we do not have much in the way of constraining site data anyway, as is often the case, the point is somewhat academic. We need to move forward within the limitations of the observations and relationships we have. Because it is the simpler and more conservative approach, the LNAPL zone will be chemically and spatially constrained using the pre-remediation thickness and the current "apparent" mole fractions in groundwater leaving that zone. The current source zone

concentration of benzene and MTBE in MW-3 is about 1 mg/l for both compounds. The corresponding apparent mole fraction of benzene is then about 5.6 x 10<sup>-4</sup>, and MTBE is about 2.1 x 10<sup>-5</sup>. Recall that this is calculated simply from the observed concentration divided by the pure phase solubility (see Section 3). For this problem, we will not concern ourselves with the details of other gasoline compounds and will simply use LNAST default values for comparative purposes.

Dilution from variable saturations and concentration distributions in the LNAPL source zone, whether caused by remediation or natural processes, presents some interesting dilemmas. For instance, it might not be appropriate to consider dilution if the discrete zone of interest were in direct contact with a groundwater receptor, as opposed to a larger aquifer thickness. This also brings up questions regarding the point of measurement and compliance; is the target cleanup concentration applied in a spatially discrete sense, or is it applied across a vertical monitoring interval or across a receptor interval? Once again, judgement about conditions and potential ramifications of the spatial position of impacts relative to receptors or points of compliance is required. At this site, ongoing commercial fuel service station use and the lack of usable groundwater because of limited production potential and poor water quality suggests that consideration of dilution is appropriate in the calculations, as there are no discrete risks from zone specific transport in the aquifer.

In summary, we have an LNAPL zone that is about 2 m thick, but no longer able to accumulate in wells (residual saturation). The source zone has been depleted of soluble components, except for an undefined interval that apparently has a composition similar to the initial source now feeding a diluted groundwater plume. The source composition will be prescribed using the "diluted" mole fraction estimates provided above. The geologic conditions will be approximated by a 2-layer condition of a silty sand overlain by a clean sand. The remaining properties will be based on the example values given in the LNAST utility or through site specific interpretation.

# 6.3.3 Running the Problem

This problem is executed in the same sequence as the prior examples. The LNAST utility is opened, and the **Soil Properties** Tab selected first. Select the *Vertically Layered Conditions* option, 2-layers (Figure 6-31). Notice that a dialog box appears where you will highlight the soil layer of interest, with Layer 1 always being the lowermost. In our problem, Layer 1 is the silty sand material with the properties given in Table 6-2, and Layer 2 is the sand, both 1m in thickness.

The groundwater gradient was given at 0.005 (**Groundwater Conditions** Tab is not shown for this problem). The LNAPL **Source Area Parameters** are selected based on the geometry and LNAPL distribution observations discussed above (Figure 6-32). The LNAPL is assumed to be at residual saturation, as it no longer accumulates above trace levels in observation wells. The saturations could



Figure 6-31. Soil Properties Tab for Problem #3, with Layer 1 shown (silty sand).

be lower than this, but we currently have no information from which to make that determination. Depending on the results of the analyses and the implications of the selected saturation values, one might choose to collect site specific data if it becomes important to know these values with more certainty.

The **LNAPL Properties** are specified next (Figure 6-33). The default example values for gasoline are used, except for the molar fractions of the compounds of interest. Recall that the apparent mole fractions of compounds in the LNAPL can be derived simply by dividing the observed concentrations in groundwater by the pure phase solubility for each compound. As discussed, this is an "apparent" mole fraction that includes the effects of dilution that are apparent in the site data. The degradation half-life for MTBE is left at 9000 days, essentially non-degraded, as a worst-case condition.

The **Solute Transport Properties** are modified with respect to dispersivity and volatilization efficiency, with other parameters left unchanged from initial default values. The longitudinal dispersivity is set to 25 m, which is about 10% of the expected field scale, the transverse dispersivity is 20% of this value (5 m), and the vertical dispersivity is 1% of the longitudinal (0.25 m). You may already recognize that the expected field scale of the plume is different for the various compounds,



Figure 6-32. Source Area Parameters Tab and selections for Problem 3.

Soil Properties	Groundwater Co	onditions Sourc	e Area Parameters		Properties	Solute Tra Propert
LNAPL Phase Pr Hydrocarbon Ty Gasoline	operties /pe ▼	Densily (	gm/cc) 0.73	. (C	lil/Water Interfacia (dynes/cn lil/Air (nterfacial T)	al Tension 🏼 🗍 II) ension 🔹 🖥
					(dynes/cm)	
					Viscosity (c	<b>pi</b> [0.62]
)issolved Phase	Properties					, 1 <u>0.02</u>
Dissolved Phase	Properties Pure Phase Solubility (mg/l)	Pure Phase Vapor Conc. (mg/l)	Mole Fraction of LNAPL	Log(Koc)	Biodegradation Half-Life (days)	Target Concentrati (ug/l)
Dissolved Phase MTBE	Properties Pure Phase Solubility (mg/l) 48000	Pure Phase Vapor Conc. (mg/l) 1204	Mole Fraction of LNAPL	Log(Koc)	Biodegradation Half-Life (days) 730	Target Concentrati (ug/l) 40
Dissolved Phase MTBE Benzene	Properties Pure Phase Solubility (mg/l) 48000 1780	Pure Phase Vapor Conc. (mg/l) 1204 324	Mole Fraction of LNAPL 0.000021 0.00056	Log(Koc) 1 2	Biodegradation Half-Life (days) 730 90	Target Concentrati (ug/l) 40 5
Dissolved Phase MTBE Benzene Ethyl Benzene	Properties Pure Phase Solubility (mg/l) 48000 1780 135	Pure Phase Vapor Conc. (mg/l) 1204 324 57	Mole Fraction of LNAPL 0.000021 0.00056 0.0013	Log(Koc) 1 2 3	Biodegradation Half-Life (days) 730 90 65	Target Concentrati (ug/l) 40 5 700
Dissolved Phase MTBE Benzene Ethyl Benzene Toluene	Properties Pure Phase Solubility (mg/l) 48000 1780 135 515	Pure Phase Vapor Conc. (mg/l) 1204 324 57 111	Mole Fraction of LNAPL 0.000021 0.00056 0.0013 0.000019	Log(Koc) 1 2 3 2,06	Biodegradation Half-Life (days) 730 90 65 60	Target Concentrati (ug/l) 40 5 700 1000
Dissolved Phase MTBE Benzene Ethyl Benzene Toluene Xylene	Properties Pure Phase Solubility (mg/l) 48000 1780 135 515 175	Pure Phase Vapor Conc. (mg/l) 1204 324 57 111 38	Mole Fraction of LNAPL 0.000021 0.00056 0.0013 0.000019 0.00045	Log(Koc) 1 2 3 2.06 2.6	Biodegradation Half-Life (days) 730 90 65 60 150	Targe Concentra (ug/l) 40 5 700 1000 10000

Figure 6-33. The **LNAPL Properties** Tab for Problem 3. The only modified properties are the mole fractions of the compounds, which were derived by dividing the currently observed dissolved-phase concentrations by the pure phase solubility of each.

primarily as a function of the degradation term. One may therefore wish to run separate calculations of potentially low degradability compounds versus higher degradability chemical species; we will not do so in this tutorial. The vapor diffusion efficiency is set to 0.01 to account for the site concrete surface cover that is in good condition. This is a typical factor used in many vapor risk screening methods, though again, if it were to become



Figure 6-34. LNAPL saturation profile for the 2-layer soil condition, silty sand overlain by sand each bed 1 m thick. Notice that the saturation condition in the silty sand is less than the residual saturation for these particular conditions.

critical to results, one would typically look closer at justifications for a site specific value.

#### 6.3.4 Results

We will again view results by first starting with the LNAPL saturation distribution and the associated groundwater flow through that zone, as this sets context for the chemical depletion and groundwater transport conditions. Recall that we specified residual saturation conditions for both geologic beds, the silty sand overlain by the sand. The associ-



Figure 6-35. Groundwater discharge through the LNAPL zone.

ated LNAPL saturation profile shows that the calculated distribution in the silty material is less than the residual saturation for this particular problem, so the profile has a sharp predicted increase in LNAPL saturation at the contact between the two soil materials (1 m elevation above the oil/water interface; Figure 6-34). This presents an interesting condition, because while the hydraulic conductivity of the silty material is much smaller than the sand, the relative permeability to water is greater in the silty material because there is much less LNAPL. The result is that the contrast in groundwater flux through the 2 beds is not as great as one might have initially suspected, though a contrast of about 20 is present (Figure 6-35). The background contrast in groundwater flux through these units would be the ratio of the conductivities, or about a factor of 60. This is another example of the sometimes non-intuitive aspects of multiphase flow. The LNAPL source depletion estimates suggest depletion times of 100 years or more for the more soluble components (Figure 6-36). This is because the averaged "diluted" mole fraction is small, and therefore mass loss rates are also small. As mentioned previously, the result would be little different if a discrete zone at full mole fractions were specified in the silty material and dilution was factored into the output information. However, if on the other hand, the "stranded" LNAPL zone were in the sandy material and not treated by the SVE because of the intervening water saturation, then depletion would be much faster (Figure 6-37). This calculation is not detailed here, but briefly was derived from the User Input Distribution option in the LNAPL properties describing a thin zone of impacts, and adjusting the mole fractions back to "non-diluted" conditions. The expected groundwater transport under the assumed problem conditions, will in large part, dictate the need to better resolve the site conceptual model. Clearly if the second condition is more representative, one should see the gross-scale verification in less than



Figure 6-36. Estimated groundwater concentration versus time at the leading edge of the LNAPL source zone (depletion curves).



Figure 6-37. Hypothetical LNAPL zone depletion of soluble compound for conditions of a discrete LNAPL interval in only the sandy zone.

1 year in the field by significantly decreasing MTBE trends in source area groundwater.

The estimated downgradient extents of the various compounds shows the importance of the degradation half-life selected for each and their target concentration (Figure 6-38). For this case, only benzene and MTBE are estimated to be present downgradient at concentrations exceeding the selected target levels. Again, this does not imply that the other components are not present, but simply that they are below the selected threshold. For the given case, MTBE is expected to reach a downgradient distance of about 100 m before the combined transport processes reduce the concentration to below the selected 40 ug/l target threshold. The estimated time to reach this distance for the given conditions is about 10 years for MTBE, whereas benzene is expected to reach is maximum downstream distance of about 42 m after about 2.5 years. For the given scenario, one can also observe that the residence time of downstream impacts for benzene is more than 100 yrs before source zone depletion starts to reduce impacts for the given conditions.

As is sometimes the case, where one goes from here depends on the specifics of the site, regulatory context, potential use conditions, and the environmental setting. From the prior discussion and evaluations, it is clear that a range of residual LNAPL impacts and chemical conditions are possible at the site following the SVE cleanup operations, none of which can be further discerned or constrained from the available information. At least now we have some conceptual models and ideas that can be tested in the field. Therefore the site context and need for further investigation rests on a few general technical considerations. First, within the zone of remaining LNAPL, vapor, and dissolvedphase impacts, it is important to consider whether those impacts pose any near-term



Figure 6-38. Estimated downgradient extents of MTBE and benzene. The other gasoline compounds of potential concern do not extend downgradient in relation to their target concentrations.



Figure 6-39. Predicted breakthrough curves for MTBE and benzene at 1 m and 10 m downgradient of LNAPL.

potential threat. If not, then continued monitoring of groundwater conditions will assist in shedding light on which of the various possible scenarios is most consistent with the monitoring data. One would typically use the range of estimated chemical trends, including breakthrough curves, in this comparison (Figure 6-39). Second, if there is no near-term threat, but the potential for long-term impacts is a concern, then a determination must be made on how continued groundwater monitoring will fold into the constraining the site conceptual models and over what timeframe before other actions would be needed. Last, if potential near-term or other impacts are unacceptable as they stand or if other factors require better resolution of the problem, then one would typically collect in situ field data to constrain key assumptions in the various conceptual models. For this case, the key data

would be the remaining LNAPL saturation distribution and its chemistry. But as one is investigating subsurface conditions, other parameters could certainly also be obtained at the same time.

This example shows that real world problems often have no immediate answer. Often the best we can do is eliminate unrealistic assumptions and conditions to assist in focussing on the key concerns and the related potential data deficiencies to improve the certainty of the analysis. A reminder: while the processes are fairly well known, the challenge lies in describing spatial distributions of parameters controlling those processes on a site specific basis. Because the processes are pore- and molecular scale, it is easy to become mired in details that have bearing, but may not be critically important. That is the importance of setting clearly defined boundaries for site conceptual models so that only useful improvements are sought, as needed. For the given case, little would be gained by trying to better constrain the groundwater gradient, general geologic setting, or transport parameters. However, as discussed at the beginning of the problem, the conceptual questions of greatest importance were where the LNAPL resides and at what saturations and chemical state.