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Enhanced Data Analysis for the VZMS: Conceptual Model Design and Initial Application for the Vadose Zone Monitoring System (VZMS), McClellan AFB 1998 Semi-Annual Report

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**Earth Sciences Division
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Berkeley, CA 94720**

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ABSTRACT

The VZMS project at McClellan AFB involves both vadose zone data collection as well as enhanced data analysis. The purpose of enhanced data analysis is to develop conceptual models to carry out model validation and evaluation, as well as sensitivity and predictive modeling studies. Enhanced data analysis consists primarily of T2VOC forward simulations and ITOUGH2 inverse modeling. The methodology we employ in the VZMS project involves developing a conceptual model and iteratively updating it based on the agreement between model results and VZMS data. We demonstrate the development of an initial T2VOC conceptual model for the S-7 site based on data from instrument cluster VZMS-B. Lithologic data from the drilling logs along with empirical relations for estimating permeability and sediment moisture retention characteristics are used to define the layering of four different sediment types. We adjusted the layering of the sediments manually until the sediment moisture content profile from the T2VOC simulation of the gravity-capillary equilibrium agreed well with observed neutron probe data. Using this updated conceptual model, we performed inverse modeling using ITOUGH2 to find best-fit absolute permeability values based on the minimization of differences between simulated and actual soil-gas pressure measurements. We determined that the T2VOC conceptual model Sandy Silt layer was the most important layer controlling pressure, and that the empirically derived value of permeability for Sandy Silt was relatively close to the best-fit value from the inverse modeling. We then iteratively updated the conceptual model to include the best-fit value of permeability for the Sandy Silt layers. The T2VOC conceptual model developed here for VZMS-B is ready for further use in evaluating hypotheses, making predictions, and carrying out sensitivity and uncertainty analyses.

1. INTRODUCTION

A Vadose Zone Monitoring System (VZMS) (LBNL, 1996) has been installed at site S-7 in IC 34, at McClellan AFB, a layout of which is presented in Figure 1. The VZMS is designed to collect detailed subsurface data over time including hydraulic potential, soil-gas pressure, moisture content, water chemistry, gas chemistry, and temperature. The VZMS data by themselves provide a detailed characterization of the site and thus could be used directly to assist in designing an effective remediation strategy. However, given the large number of contaminated sites at McClellan AFB, it would be impractical to collect detailed VZMS data at more than a handful of sites. Thus, the majority of sites must rely on modeling studies to assist in characterization and remediation design. Although great improvements in modeling capabilities

have been made over the last 10 years, modeling results alone are typically not sufficient to design effective remediation strategies or to satisfy regulatory agencies. For model results to be defensible, they need to be based on actual site data and have credible predictive capability. The purpose of the VZMS project being carried out by LBNL and McClellan AFB is to collect detailed data and perform enhanced data analysis for model validation and evaluation. In addition, the enhanced data analysis can be used for sensitivity analyses to determine which properties most strongly control important aspects of system behavior, such as the downward flux of contaminants. The investment made in the VZMS project will lead to future cost savings at other sites by enabling defensible risk analysis and remediation design through modeling, as well as by allowing more focused site characterization studies to be performed. In this report we present the VZMS enhanced data analysis approach through its first application using pressure data to constrain and validate permeability structure.

2. ENHANCED DATA ANALYSIS

Prior to presenting the actual application of enhanced data analysis carried out for the VZMS at S-7, we provide here a brief overview of the methodology. Broadly, the enhanced data analysis for VZMS data involves developing a conceptual model for the site, implementing the conceptual model into a numerical simulator, carrying out numerical simulation studies, and then iteratively updating the conceptual model. This iterative methodology is shown schematically in Figure 2. The process starts with the collection of site data, for example from borehole drilling and well monitoring along with the broader knowledge developed over time at a site. Interpretations of these data provide the information necessary to develop an initial conceptual model. Next, the conceptual model is implemented into a numerical model, in this case the three-dimensional multiphase (gas, aqueous, NAPL) and multicomponent (air, water, VOC) integral finite difference simulator T2VOC (Falta et al., 1995; 1992a; 1992b). The processes and methods used in T2VOC are described in Appendix A. The numerical model T2VOC requires the conceptual model to be defined by a computational domain with boundary and initial conditions, as well as physical properties such as porosity and permeability. Once implemented into T2VOC, we refer to the conceptual model as the T2VOC conceptual model. The T2VOC simulator can then be applied to carry out forward simulations to make predictions of moisture migration, pressure response, or the transport of VOCs, for example. One way of using these predictions is to compare them to the VZMS data that are collected over time. When deviations between observed and calculated results arise, the T2VOC conceptual model properties or boundary conditions can be adjusted to improve the predictions. In the enhanced data analysis

Figure 1. Location of VZMS installations relative to existing and former structures at Site S-7, including locations of previously drilled boreholes and soil-gas sampling points.

for the VZMS, we employ the inverse modeling code ITOUGH2 (Finsterle, 1995) which can automatically adjust property values until differences between observed and calculated values are minimized. The methods used in ITOUGH2 are described in Appendix B. As shown in Figure 2, the simulation predictions can be used alone for remediation design or risk analysis, or compared with observations from the VZMS. The iterative updating based on agreement between predictions and VZMS data results in a T2VOC conceptual model that is based on all of the data available. We emphasize that the T2VOC conceptual model is an averaged model that is based on information from many sources. As such, the T2VOC conceptual model will generally not exactly match data from every source in every respect.

The resulting T2VOC conceptual model is used in the enhanced data analysis to quantify interpretations, test hypotheses, and perform uncertainty and sensitivity analyses. Specifically, we can perform numerical experiments to quantify and test the causes of trends observed in the data. Similarly, we can perform sensitivity analyses to determine which properties of the system most strongly influence system behavior. This information can lead to more efficient site characterization that is focused on obtaining values of the most important properties of the system. Simulation results from the T2VOC conceptual model can also be used to show regulatory agencies the ranges of possible contaminant fluxes given the inherent uncertainty in the many subsurface property values. Finally, the results of our enhanced data analysis can be compared to prior or new modeling results obtained with other, possibly simpler, numerical models. Credibility will be given to these simpler models if they produce results consistent with VZMS data and T2VOC conceptual model results. If the results differ, improvements in model property values or process modeling capabilities of these simpler models can be made.

As discussed above, the bulk of enhanced data analysis is numerical simulation studies, which comprise the whole set of T2VOC forward calculations as well as the ITOUGH2 inverse, sensitivity, and uncertainty calculations. As we will show in the application below, there is a tight coupling between VZMS data and the enhanced data analysis. This relation between VZMS data and enhanced data analysis will be made transparent in the application presented in the remainder of this report.

Figure 2. Schematic of the enhanced data analysis iterative loop.

3. CONCEPTUAL MODEL DEVELOPMENT

3.1 Introduction

An initial conceptual model was developed using the various types of site data collected during VZMS installation described by Zawislanski et al. (LBNL, 1996). Generally, the subsurface at site S-7 is conceptualized as a thick section of dry to moist alluvial sediments variably contaminated by VOCs. The alluvium consists of interbedded, poorly-graded sand and silt layers with thin and sparse gravel and clay layers. The water table is located at a depth of approximately 110 ft. The system is bounded at the top by a paved surface at atmospheric pressure and temperature and at the bottom by the water table. Water can infiltrate the subsurface due to rainfall events, and drying of the shallow subsurface can occur during dry periods. The direction of contaminant migration is under investigation, but preliminary data point toward both downward and upward fluxes of VOCs being possible by gas phase advection and diffusion. We assume that the predominant direction of flow and transport is vertical.

Available hydrostratigraphic site-specific data include lithologic logs collected during drilling, physical parameter and particle size analysis of split-spoon samples, and neutron probe measurements of sediment moisture content at depth (LBNL, 1996). In this report, these data will be used in the estimation of hydrogeologic parameters fundamental to the description of subsurface flow and transport. Particle size analysis was performed on representative sediment samples to give values of percent sand, silt, and clay for each sample. Sediment samples were also analyzed for physical properties of moisture content, bulk density, specific gravity, porosity, and total organic carbon. The particle size analysis and the physical property analysis were performed on different samples that did not necessarily coincide in depth. However, the results did provide a range of depths at which both analyses were performed, allowing for the estimation of hydraulic properties based on measured physical sediment properties. The hydrogeologic properties that result from the estimation process described here are provided for VZMS-B only. Future modeling work will include information from both VZMS-A and VZMS-B.

3.2 Absolute Permeability

Hydrogeologic properties of sediments can be estimated from physical and characteristic properties such as particle size distributions, bulk density, porosity, and carbon content (Jabro, 1992; Shepherd, 1989; Bear, 1972; Freeze and Cherry, 1979; Wösten and van Genuchten, 1988; Rawls et al., 1991; Vereecken et al., 1992). In this work, estimates of permeability were obtained using empirical relationships provided by Bear (1972) and Jabro (1992). From Bear (1972)

(Method 1), the Kozeny-Carmen equation relates permeability to porosity and mean particle size for a porous medium conceptualized as a bundle of equal length capillary tubes such that

$$k = \frac{d^2}{180} \cdot \frac{n^3}{(1-n)^2} \quad (1)$$

where

k = permeability, [μm^2]

n = porosity

d = mean particle size, [μm^2].

Before a value of permeability can be evaluated, an estimate for the mean particle size of the sediment is required. Shiozawa and Campbell (1991) derived an expression relating sand, silt, and clay fractions to a geometric mean particle diameter based on the analysis of six Washington State soils. Their equation is

$$d = \exp[5.756 - 3.454(f_{\text{silt}}) - 7.712(f_{\text{clay}})] \quad (2)$$

where

d = geometric mean particle diameter, [μm]

f_{silt} = fraction of silt

f_{clay} = fraction of clay.

As a comparison we also used the following relationship of Jabro (1992) (Method 2) to relate saturated hydraulic conductivity as a direct function of percent silt, percent clay, and bulk density:

$$\log(K_s) = 9.56 - 0.81\log(\% \text{silt}) - 1.09\log(\% \text{clay}) - 4.64(bd) \quad (3)$$

where

K_s = saturated hydraulic conductivity, [cm/h]

bd = bulk density, [g/cm^3].

In the development of this model, Jabro used published data from 350 core samples of various soils.

Table 1 lists the estimates of permeability at the selected depths for both Method 1 (Bear, 1972; Shiozawa and Campbell, 1991) and Method 2 (Jabro, 1992). Estimates using Method 1 were up to 2.5 orders of magnitude higher than those provided by Method 2 with the exception of permeability values for the clean sand. For clean sand, Method 1 estimated a permeability of 275 darcies ($k = 2.75 \times 10^{-10} \text{ m}^2$) while Method 2 gave a value of 1445 darcies ($k = 1.445 \times 10^{-9} \text{ m}^2$). The estimates provided in Table 1 were used to define sediment layers characteristic of the subsurface in VZMS-B, and are defined in the following subsection entitled "T2VOC Conceptual Model".

3.3 Sediment Moisture Retention

Rawls et al. (1991) give a description of the various approaches for estimating sediment water retention from sediment physical properties and characteristics. In their review, they include the work of Vereecken (1988), where the well-known van Genuchten model (van Genuchten, 1980) is fit to data using a regression analysis to relate model parameters to sediment properties. The analysis resulted in the following expressions for the van Genuchten parameters:

$$\theta_r = 0.015 + 0.005(\% \text{clay}) + 0.014(\% \text{carbon}) \quad (4)$$

$$\alpha = \exp[-2.486 + 0.025(\% \text{sand}) - 0.351(\% \text{carbon}) - 2.617(\text{bd}) - 0.023(\% \text{clay})] \quad (5)$$

$$n = \exp[0.053 - 0.009(\% \text{sand}) - 0.013(\% \text{clay}) + 0.00015(\% \text{sand})^2] \quad (6)$$

$$m = 1 - \frac{1}{n} \quad (7)$$

where

θ_r = residual moisture content

bd = bulk density, $[\text{g}/\text{cm}^3]$

$1/\alpha$ = air entry pressure, $[\text{cm}]$

n = pore-size distribution index.

Alongside the permeability estimates, Table 1 lists the van Genuchten parameters obtained using Vereecken's (1988) equations and the proportions of clay, sand, and carbon for each sediment sample/depth. In Figures 3 and 4, we show the modeled van Genuchten moisture retention and liquid phase relative permeability curves, respectively, for the selected depths in VZMS-B. It is important to note that the relationships used here to transform sediment physical and characteristic curve properties into descriptive hydrogeologic parameters are based on regression

analysis of a range of sediments and thus are average relationships. Therefore, these relationships may be limited in their ability to accurately estimate parameters for any one site.

Table 1. Hydrogeologic parameter estimates for selected depths in VZMS-B.

VZMS B - sediments			Intrinsic permeability		van Genuchten parameters	
Sediment Type	Sediment Description	depth (ft)	Method 1 log k [m ²]	Method 2 log k [m ²]	1/ α [Pa]	n
SM	silty sand	7	-9.9	-11.3	7300	1.3
ML	sandy silt	18.5	-11.2	-13.4	33700	1
SM	silty sand	28.5	-11.3	-12.3	25800	1
SM	silty sand	33.5	-10.8	-12.9	29300	1.1
SM-SL	silty-clayey sand	38.5	-10.8	-12.9	27500	1.1
SM	silty sand	58.5	-10.7	-13.1	21700	1.4
SP-SW	clean sand	98.5	-9.5	-8.8	3800	1.9

3.4 T2VOC Conceptual Model

The preliminary conceptual model must be implemented into a T2VOC conceptual model for enhanced data analysis. Because we assume that the predominant direction of flow and transport is vertical, we have chosen to begin modeling efforts by carrying out a one-dimensional simulation for borehole VZMS-B. Selection of VZMS-B was based on the availability of full depth neutron probe data for the adjacent borehole NP-B (see Figure 1) down to the water table (borehole NP-A remains obstructed at a depth of approximately 25 ft). We define the physical domain as a one-dimensional sediment column bounded above by atmospheric pressure and below by the water table. The 100 ft column is discretized into 200 gridblocks, each half a foot (0.1524 m) in thickness. The atmospheric pressure boundary is variable through time and exactly mimics the atmospheric pressure data recorded from on-site pressure transducers.

From the site-specific estimates of permeability and sediment moisture retention shown in Figures 3 and 4, we differentiate four generalized sediment layers, characteristic of the subsurface layers found in VZMS-B. These four sediment types are then used to describe the hydrostratigraphy throughout the column according to the corresponding lithologic log. Table 2 provides the values of the hydrogeologic parameters defining the four sediment types, including permeability and van Genuchten parameters. Silty Sand 1 is based on the sediment sample at

Figure 3. Estimated van Genuchten sediment moisture retention curves at selected depths for VZMS-B.

Figure 4. van Genuchten liquid phase relative permeability curves at selected depths for VZMS-B.

depth 7 ft. Layer Sandy Silt averages properties from depths 18.5 ft to 38.5 ft. Silty Sand 2 and Sand reflect sediment properties at depths of 58.5 and 98.5 ft, respectively. The lower estimates of permeability provided by Method 2 (Jabro, 1992) were used to describe the permeabilities of the defined sediments, with the exception of layer Sand where Method 1 (Bear, 1972; Shiozawa and Campbell, 1991) provided a smaller estimate of k . A fifth sediment layer, defined as concrete, describes the top 3 ft of VZMS-B. The physical properties of the concrete are assumed to be the same as Silty Sand 1 with a somewhat reduced permeability of 1 darcy or $\log(k[\text{m}^2]) = -12.0$. Figures 5 and 6 illustrate the defined sediment layer van Genuchten moisture retention and liquid phase relative permeability curves, respectively. Comparison of Figures 3 and 5, as well as Figures 4 and 6, show how we grouped the actual sediments into the model properties selected for the T2VOC conceptual model.

Table 2. Defined sediment layers and hydrogeologic parameters for VZMS-B.

Sediment Name	$\phi^\dagger$	$\rho^\dagger$ [kg/m ³]	$\log k$ [m ²]	$1/\alpha$ [Pa]	n	$S_r^\dagger$	FOC †
Silty Sand 1	.57	1448	-11.3	7300	1.32	.066	.015
Sandy Silt	.45	1781	-12.9	29000	1.1	.07	.012
Silty Sand 2	.38	1879	-13.2	22000	1.35	.077	.005
Sand	.51	1384	-9.6	3800	1.87	.04	.005

† ϕ = porosity, ρ = bulk density, S_r = residual liquid saturation, FOC = fraction organic carbon

3.5 Conceptual Model Validation

A steady-state moisture profile within the column was created by saturating the T2VOC conceptual model and allowing the liquid phase to redistribute itself by gravity and capillary forces. The simulated moisture content profile was qualitatively compared to the profile derived from the neutron probe data of NP-B included in the 1997 VZMS Annual Report (LBNL, 1998). Upon comparing the actual data to this initial T2VOC simulation, we observed good agreement for the lower 50 ft of the column. A less satisfactory match in the upper 50 ft suggested that a larger number of characteristic sediments may be required to fully describe this section of the column. Nine samples collected from a new borehole drilled nearby in April 1998 are currently being analyzed for saturated and unsaturated hydrologic properties. In future simulations, this new information will provide a stronger basis for the discretization of sediment layers. For the purpose of these initial simulations, we manually adjusted the distribution of the four sediment layers within the upper section of the column in the T2VOC conceptual model and repeated the steady-state simulation. A more satisfactory match of the moisture content profile was obtained

and can be seen in Figure 7. It is important to note that the T2VOC conceptual model is intended to be an abstraction of the actual system and is based on data from VZMS-B, NP-B, as well as empirical correlations. Therefore, we do not require the T2VOC conceptual model to exactly match data from any one source. Good qualitative agreement between the moisture content as measured by neutron probe in NP-B and simulated for the T2VOC conceptual model based on lithology in VZMS-B provides significant validation of the conceptual model. Figure 8 shows the actual lithologic log for VZMS-B next to the final T2VOC conceptual model lithology for comparison. The steady-state moisture profile is used as initial conditions for the subsequent application work. With confidence in the hydrostratigraphic description of the subsurface at VZMS-B, the T2VOC conceptual model can be used to predict and validate system behavior such as formation pressure response to a temporally changing atmospheric pressure boundary, as described in the following section.

Figure 5. van Genuchten moisture retention curves for the four sediment layers in VZMS-B.

Figure 6. van Genuchten relative permeability curves for the four sediment layers in VZMS-B.

Figure 7. Comparison of simulated and neutron-probe-derived moisture content profiles in VZMS-B.

Figure 8. Comparison of actual lithologic log and T2VOC conceptual model in VZMS-B.

Figure 8. Comparison of actual lithologic log and T2VOC conceptual model in VZMS-B (continued).

4. PRELIMINARY APPLICATION

4.1 Introduction

In this section, the T2VOC conceptual model is used in an application to predict the response of formation pressure at depth to the temporal fluctuations in the atmospheric pressure boundary condition. The objective of this application is to determine absolute permeability values for the T2VOC conceptual model. The extensive data for both atmospheric and formation gas pressure continuously collected by the VZMS allow for a detailed comparison between data and T2VOC model predictions and the matching of these predictions using the inverse modeling capabilities of ITOUGH2 (Finsterle, 1997a). The forward T2VOC simulations run from 5/21/97 to 11/20/97 (Julian day 141 to 320). Readings of atmospheric and formation gas pressure have been taken on 4-hour intervals over this entire period. The atmospheric pressure boundary condition used in the T2VOC simulations mimics these data. Figure 9 illustrates the temporal variation in this boundary condition over the entire simulation. For ease of analysis, simulation results of formation pressure at depth are compared to data over a single week, from 11/6/97 to 11/13/97 (Julian day 310 to 317). Because site contaminant concentration profiles have shown the top 30 ft of the subsurface to be the area of greatest contamination and since response to atmospheric pressure variation will be strongest at shallow depth, only the top 4 sensor levels (6 ft, 11 ft, 18 ft and 30 ft) are used in this analysis. Furthermore, we expect VOC movement to be most significantly affected by gas-phase flow within the top 30 ft of the sediment column.

4.2 Inversion for Calibration Offset

Figure 10 shows data (symbols) and the forward simulation results (solid lines) of atmospheric and formation pressure (6 ft, 11 ft, 18 ft and 30 ft) from 11/6/97 to 11/13/97. All depths respond quickly to atmospheric pressure changes. When simulated formation pressure is averaged and interpolated, as was done by Zawislanski and Oldenburg (LBNL, 1998), the simulated lag between atmospheric and depth appears to match the VZMS data. However, differences between data and simulation results are observed in the absolute value of formation pressure at any point in time. Simulation results give an expected increase in pressure with depth consistent with a gas-static profile. In contrast, some of the VZMS pressure data show lower pressures at greater depths than at shallower depths, a relation not expected in a relatively permeable vadose zone. This discrepancy between data and simulated absolute formation pressures could potentially be attributed to uncertainty in field measurements introduced by instrumentation calibration. The pressure transducer calibration uncertainty is ± 0.004 bar (400 Pa) (LBNL, 1998).

Figure 9. Atmospheric pressure boundary condition applied from 5/21/97 to 11/20/97 (Julian day 141-320).

Figure 10. Atmospheric pressure and formation pressure at depth in VZMS-B from 11/6/97 to 11/13/97 (Julian day 310 to 317). Data collected on a 4-hour interval (symbols). Forward simulation results (solid lines) were obtained using 170 days of atmospheric pressure history (see Figure 9).

To account for the uncertainty in instrument calibration, an ITOUGH2 inversion was performed to independently estimate a calibration offset for each data set. Numerical matching of data and simulation was performed over the single week of data. Table 3 gives the initial guesses and final inversion results for the value of the constant by which pressures from each data set are reduced to optimally fit the forward simulation. By performing this inversion, we are postulating that each data set collected contains a constant offset whose value is determined by the calibration. All four estimated values of the calibration offset are within the 0.004 bar (400 Pa) margin of uncertainty, and as a result, we feel this interpretation is a likely explanation for why the data do not reflect a gas-static profile. Figure 11 shows for each depth the collected data (symbols), the original forward simulation (solid line) and the new simulation encompassing the added offset (dotted line) due to calibration uncertainty.

Table 3. Initial guess and inversion results of calibration offset.

Data Depth [ft]	Initial Guess [Pa]	Inversion Result [Pa]
6 ft	300	237
11 ft	300	286
18 ft	-300	-246
30 ft	300	179

4.3 Inversion for Absolute Permeability

A second inversion was performed to investigate the appropriateness of the sediment layer permeabilities, the estimation methodology for which was described in section 3.2. An initial inversion allowed permeability values of layers Silty Sand 1, Silty Sand 2, Sandy Silt, and Concrete to change in order to better match data at all four depths over the one-week period. The sediment layer Sand was excluded as a parameter in the inversion because it appears only at depths of 85 ft and below. Results of this initial inversion indicated that the match between data and simulation was insensitive to the permeability of layers Silty Sand 1 and Silty Sand 2. This conclusion was not surprising since three of the four instrumented depths used in the inversion reside within the T2VOC conceptual model layer Sandy Silt, and the fourth instrumented depth, in layer Silty Sand 1, is bounded above and below by Sandy Silt (see Figure 8 for corresponding model lithology at depths of 6 ft, 11 ft, 18 ft and 30 ft). The inversion was repeated, defining variable permeabilities for Sandy Silt and Concrete. Table 4 lists the initial guesses and inversion results for these two permeabilities. The permeability of layer Sandy Silt was by far the most

important parameter. However, the inversion results, illustrated in Figure 12, show that little improvement was made on the matches obtained between the forward run with calibration offset and data. The final permeability of layer Sandy Silt is not very different from the value estimated from site data, leading us to conclude that the methodology of constructing the initial conceptual model described in section 3.0 provided a good initial guess of permeability.

Table 4. Initial guess and inversion results of permeability values.

Defined Sediment	Initial Guess	Inversion Result
Layer	$\log(k[m^2])$	$\log(k[m^2])$
Concrete	-12.0	-13.42
Sandy Silt	-12.9	-12.74

5.0 SUMMARY

This report describes the methodology of conceptual model development and enhanced data analysis carried out for the VZMS project at McClellan AFB. In the VZMS methodology, site data are used to formulate an initial conceptual model of the site encompassing general site knowledge, subsurface lithology, hydrostratigraphy and estimates of hydrogeologic properties from empirical relations. The conceptual model is transformed into a T2VOC conceptual model that can be used for enhanced data analysis involving numerical modeling with T2VOC and ITOUGH2. In this report, a one-dimensional T2VOC conceptual model of VZMS-B is defined specifically to predict formation pressure response at depth to a temporal varying atmospheric pressure boundary condition. Comparison of the forward simulation to VZMS data allowed the estimation of individual pressure transducer calibration offsets using the inverse modeling techniques of ITOUGH2. All estimated offsets were within the uncertainty of transducer calibrations of ± 0.004 bar (400 Pa), leading us to the conclusion that this was a reasonable explanation for a non-gas-static profile in the VZMS formation pressure data. Inversion results of sediment permeability identified the T2VOC conceptual model layer Sandy Silt to be the most sensitive sediment layer. This conclusion appears reasonable given that all four data collection intervals are within or bounded by this sediment type. Inversion of permeability did not provide a significant improvement in the fit of simulation to data. This can be attributed to the relatively good permeability structure in the initial conceptual model as derived from the empirical relations. The T2VOC conceptual model developed here for VZMS-B is ready for use in evaluating hypotheses, making predictions, and carrying out sensitivity and uncertainty analyses.

Figure 11. Formation pressure at depth in VZMS-B with an independent calibration offset estimated for each data set. Data are indicated by symbols. The original forward simulation is shown by the solid line. Simulation with the estimated calibration offset is shown by the dotted line.

Figure 12. Formation pressure at depth in VZMS-B with inverted permeability values and calibration offset. Data are indicated by symbols. The forward simulation with the calibration offset is shown by the solid line. Simulation with calibration offset and inverted permeabilities is shown by the dotted line.

APPENDIX A.

T2VOC

A.1 Introduction

T2VOC is a numerical simulation program for modeling the transport of organic chemical contaminants in nonisothermal multiphase systems. T2VOC is the three-phase version of the TOUGH2 simulator (Pruess, 1987, 1991). The TOUGH codes (transport of **u**nsaturated groundwater and **h**eat) are three-dimensional codes for simulating the coupled transport of water, water vapor, air, and heat in porous and fractured porous media. The T2VOC code includes the option of a third non-aqueous phase liquid (NAPL) and was designed to simulate processes such as the migration of hazardous NAPLs in variably saturated media, forced vacuum extraction of organic chemical vapors from the unsaturated zone (soil vapor extraction), evaporation and diffusion of chemical vapors in the unsaturated zone, air injection into the saturated zone for removal of volatile organics (air sparging), direct pumping of contaminated water and free product, and steam injection for the removal of NAPLs from contaminated soils and aquifers. T2VOC uses a general integral finite difference formulation for multiphase, multi-component mass and energy balance equations. This appendix contains a summary description of the physical processes and mathematical formulation of the T2VOC simulator. A complete description of the code and instructions for preparing input files and illustrative sample problems are provided in the User's Manual (Falta et al., 1995). Descriptions and further information can also be found at <http://ccs.lbl.gov/TOUGH2>.

A.2 Physical Processes and Assumptions

In the T2VOC formulation, the multiphase system is assumed to be composed of three mass components: air, water, and a volatile, water-soluble organic chemical. Although air consists of several components (nitrogen, oxygen, etc.), it is here treated as a single "pseudo-component" with averaged properties. The three fluid components in T2VOC may be present in different proportions in any of the three phases, gas, aqueous, and NAPL, except that the (usually) small solubility of water in the NAPL phase has been neglected. T2VOC is applicable not only to slightly but also to strongly water-soluble organic compounds. The phases and components considered by the T2VOC simulator are listed in Table A.1, where the dominant component in each of the three phases is shown with a bold X.

Table A.1. T2VOC Fluid Phases and Components

Phases <i>Components</i>	gas	aqueous	NAPL
<i>water</i>	X	X	---
<i>air</i>	X	X	X
<i>VOC</i> [†]	X	X	X

[†] VOC = volatile organic compound

In addition, VOC may be adsorbed by the porous medium. Each phase flows in response to pressure and gravitational forces according to the multiphase extension of Darcy's law, including the effects of relative permeability and capillary pressure between the phases. Transport of the three mass components also occurs by multicomponent diffusion in the gas phase. It is assumed that the three phases are in local chemical and thermal equilibrium, and that no chemical reactions are taking place other than (a) interphase mass transfer, (b) adsorption of the chemical component to the solid phase, and (c) decay of VOC by biodegradation. Mechanisms of interphase mass transfer for the organic chemical component include evaporation and boiling of the NAPL, dissolution of the NAPL into the aqueous phase, condensation of the organic chemical from the gas phase into the NAPL, and equilibrium phase partitioning of the organic chemical between the gas, aqueous, and solid phases. Interphase mass transfer of the water component includes the effects of evaporation and boiling of the aqueous phase, and condensation of water vapor from the gas phase. The interphase mass transfer of the air component consists of equilibrium phase partitioning of the air between the gas, aqueous, and NAPL phases.

Heat transfer occurs due to conduction, multiphase convection, and gaseous diffusion. The heat transfer effects of phase transitions between the NAPL, aqueous and gas phases are fully accounted for by considering the transport of both latent and sensible heat. The overall porous media thermal conductivity is calculated as a function of water and NAPL saturation, and depends on the chemical characteristics of the NAPL.

Water properties in the liquid and vapor state are calculated, within experimental accuracy, from the steam table equations given by the International Formulation Committee (1967). Thermophysical properties of the NAPL phase such as saturated vapor pressure and viscosity are calculated as functions of temperature, while specific enthalpy and density are computed as functions of both temperature and pressure. Vapor pressure lowering effects due to capillary forces are not presently included in the simulator. Gas phase thermophysical properties such as specific

enthalpy, viscosity, density, and component molecular diffusivities are considered to be functions of temperature, pressure, and gas phase composition. The solubility of the organic chemical in water may be specified as a function of temperature, and Henry's constant for dissolution of organic chemical vapors in the aqueous phase is calculated as a function of temperature. The Henry's constants for air dissolution in aqueous and NAPL phases are small and for simplicity have been assumed to be constant.

The necessary NAPL/organic chemical thermophysical and transport properties are computed by means of a very general equation of state. This equation of state is largely based on semi-empirical corresponding states methods in which chemical parameters are calculated as functions of the critical properties of the chemical such as the critical temperature and pressure. Because these data are available for hundreds of organic compounds, the NAPL/organic chemical equation of state is quite flexible in its application.

By virtue of the fact that the integral finite difference method (Narasimhan and Witherspoon, 1976) is used for spatial discretization, the formulation of T2VOC makes no reference to a global coordinate system, and no particular dimensionality is required. The T2VOC simulator may therefore be used for one, two, or three-dimensional anisotropic, heterogeneous porous or fractured systems having complex geometries. The porous medium porosity may be specified to be a function of pore pressure and temperature, but no stress calculations are made.

T2VOC assembles a set of nonlinear coupled integral mass balance equations that are discretized in space and time. Space is discretized with the integral finite difference method, which for regular grid systems is mathematically equivalent to conventional finite difference method, but offers added geometric flexibility. Time differencing is made fully implicitly, using first-order backward finite differences. For a flow system with N grid blocks and NEQ balance equations per block, discretization results in a system of $N * NEQ$ coupled non-linear algebraic equations which is solved by Newton-Raphson iteration. The linear equations arising at each iteration step are solved by means of iterative pre-conditioned conjugate gradient techniques (Moridis and Pruess, 1995). T2VOC uses a fully coupled residual formulation assuring convergence and mass balance at each time step.

A.3 Initial and Boundary Conditions

Flow systems are initialized by assigning a complete set of primary thermodynamic variables to each grid block. Default conditions can be assigned to the entire flow domain. These defaults can be overwritten by assigning specific conditions to certain domains, which in turn may be superseded by assigning specific thermodynamic conditions to individual grid blocks. The primary variables depend on the fluid phase composition and will generally be different in different grid blocks.

Simulation of environmental contamination and remediation problems proceeds in several steps. A first step often involves preparation of a "natural" state, prior to the contamination, for the flow system under study. This state may correspond to gravity-capillary equilibrium, with or without water infiltration, or it may be a dynamic state of regional flow. Such a model of a "natural" state may be simulated by assigning more or less arbitrary initial conditions, then imposing appropriate boundary conditions (see below), and running the flow system to a state of static or dynamic equilibrium. Pre-contamination conditions can be efficiently simulated by running T2VOC in "two-component mode", with only water and air present. The thermodynamic conditions calculated for this state consist of a complete list of all primary thermodynamic variables for all grid blocks, which is written out as a disk file called "SAVE" at the end of a T2VOC simulation run. This data may be provided as initial conditions for a subsequent second simulation run which models the release and spreading of contaminant. The thermodynamic conditions calculated in this second simulation step may be provided as initial conditions to a third step in which different remediation operations are modeled that involve injection and extraction of fluids and heat.

Boundary conditions are basically of two types, Neumann (prescribed fluxes) or Dirichlet (prescribed thermodynamic variables, such as pressure, temperature, etc.). "No flux" boundary conditions are implemented simply by not introducing any interface that could carry flow at the desired "no flux" boundary. More general Neumann boundary conditions are specified by introducing appropriate sinks or sources in the flow domain, which are placed in grid blocks adjacent to the desired flux boundary.

Dirichlet conditions can be implemented by assigning very large volumes (e.g., $V = 10^{50} \text{ m}^3$) to grid blocks adjacent to the boundary so that their thermodynamic conditions do not change at all from fluid or heat exchange with "finite-size" blocks in the flow domain. In addition, a "small" value should be specified for the nodal distance of such blocks, so that boundary conditions are maintained at the surface where they are desired and not at some distance from it. Time-dependent Neumann conditions can be specified by making sink and source rates time dependent. Time-dependent Dirichlet conditions can also be implemented; these are realized by placing appropriate sinks or sources in the "boundary blocks".

A.4 Primary Variables

In order to describe the thermodynamic state of a four-component (three mass components and heat) system in which local thermal and chemical phase equilibrium is assumed, it is necessary to choose four primary variables. In addition to the four primary variables, a complete set of "secondary parameters" is needed for the solution of the four coupled balance equations. These secondary parameters include thermodynamic and transport properties such as enthalpies,

densities, relative permeabilities, viscosities, and mass fractions. The four primary variables must be chosen to be independent so that the entire set of secondary parameters may be calculated as functions of the primary variables. The primary variables used in T2VOC are presented in Table A.2.

Table A.2. Choice of Primary Variables in T2VOC.

Phases	Primary Variables			
	<i>X1</i>	<i>X2</i>	<i>X3</i>	<i>X4</i>
1 aqueous	<i>P</i>	<i>Xaw+50</i>	<i>Xmolog</i>	<i>T</i>
2 aq., NAPL	<i>P</i>	<i>Sw</i>	<i>Xaw+50</i>	<i>T</i>
2 aq., gas	<i>P</i>	<i>Sw</i>	<i>Xmolog</i>	<i>T</i>
3 aq., gas, NAPL	<i>P</i>	<i>Sw</i>	<i>Sg+10</i>	<i>T</i>

In multiphase flow problems involving phase transitions (i.e. appearance or disappearance of a phase), the number of possible phase combinations may become large. In a system in which a maximum of three fluid phases may be present, there are seven possible phase combinations. These combinations include three single phase systems (i.e., gas, aqueous, NAPL), three two-phase systems (i.e., gas-aqueous, gas-NAPL, aqueous-NAPL), and one three-phase system (i.e., gas-aqueous-NAPL). Figure A.1 shows the phase conditions that may be described with T2VOC. Arrows indicate appearance or disappearance of phases.

Figure A.1. Fluid Phase Conditions in T2VOC.

T2VOC optionally offers the capability to solve only 2 mass balance equations, for water and air, omitting the VOC mass balance. This feature is useful for preparing "natural states" in saturated or unsaturated flow systems, prior to release of contaminant. Possible phase compositions are either single-phase aqueous, or two-phase aqueous-gas. T2VOC can also be run in isothermal mode, which reduces the number of balance equations per grid block by one and provides considerable savings in computational work. When running isothermally the user must still provide temperature assignments just as for non-isothermal calculations; however, no heat balance equation will be solved and temperatures will automatically be maintained constant during a simulation.

A.5 Secondary Parameters

In non-isothermal multiphase flow simulations, major nonlinearities in the governing equations occur due to large variations of secondary thermodynamic and transport parameters that arise from changes in the values of the primary variables. For this reason, the accurate calculation of secondary parameters from the primary variables is of considerable importance. In the formulation of T2VOC an effort has been made to include all of the parametric dependencies which significantly contribute to the nonlinearity of the problem. A complete list of all secondary parameters along with their dependence on the primary variables is given in Table A.3. The dependence of the secondary parameters on specific primary variables may change under different phase conditions due to the primary variable switching.

Table A.3. Secondary Variables and Functional Dependence

Parameter	Phase		
	gas	aqueous	NAPL
Saturation	$S_g(S_w)$	S_w	$S_n(S_w, S_g)$
Relative Permeability	$k_{rg}(S_g, S_w)$	$k_{rw}(S_w)$	$k_{rn}(S_g, S_w)$
Viscosity	$\mu_g(P, \chi_g^c, T)$	$\mu_w(P, T)$	$\mu_n(P, T)$
Density	$\rho_g(P, \chi_g^c, T)$	$\rho_w(P, T, \chi_g^c)$	$\rho_n(P, T)$
Specific Enthalpy	$h_g(P, \chi_g^c, T)$	$h_w(P, T)$	$h_n(P, T)$
Capillary Pressure	---	$P_{cgw}(S_g, S_w)$	$P_{cgn}(S_g, S_w)$
Water Mass Fraction	$X_g^w(P, \chi_g^c, T)$	$X_w^w(P, \chi_g^c, T)$	$X_n^w(P, \chi_g^c, T)$
Air Mass Fraction	$X_g^a(P, \chi_g^c, T)$	$X_w^a(P, \chi_g^c, T)$	$X_n^a(P, \chi_g^c, T)$

VOC Mass Fraction	$X_g^c(P, \chi_g^c, T)$	$X_w^c(P, \chi_g^c, T)$	$X_n^c(P, \chi_g^c, T)$
Vapor Molecular Diffusivity	$D_g^w(P, \chi_g^c, T)$	---	---
VOC Molecular Diffusivity	$D_g^c(P, \chi_g^c, T)$	---	---
Tortuosity	$\tau_g(S_g, S_w)$	---	---
VOC Henry's Constant	H_{gw}^c		
Thermal Conductivity	$K(S_g, S_w, T)$		

A.6 Summary

T2VOC is a powerful and flexible numerical simulator for modeling complex physical processes associated with multiphase flow in the subsurface. Nevertheless, T2VOC retains the conceptual simplicity of the integral finite difference method upon which it is based. Because T2VOC is part of the TOUGH family of codes, T2VOC can be coupled with ITOUGH2 to perform inverse modeling analyses.

APPENDIX B.

ITOUGH2

B.1 Introduction

The ITOUGH2 code provides inverse modeling capabilities for the TOUGH2 family of codes of which T2VOC is a member. The main purpose of ITOUGH2 is to estimate model-related parameters by automatically calibrating T2VOC conceptual models to laboratory or field data. ITOUGH2 supports three related application modes: (1) sensitivity analysis; (2) parameter estimation; and (3) uncertainty analysis. All T2VOC input parameters can be considered unknown or uncertain. The parameters are estimated based on any type of observation for which a corresponding T2VOC output is available, including prior information about the parameters to be estimated. A number of different objective functions and minimization algorithms are available. One of the key features of ITOUGH2 is its extensive error analysis which provides statistical information about residuals, estimation uncertainties, and the ability to discriminate among model alternatives. The impact of parameter uncertainties on model predictions can be studied by means of linear uncertainty propagation analysis or

Monte Carlo simulations. In this appendix, we present a brief summary of the methods used in ITOUGH2. Further information is available in Finsterle (1997a,b) and at the website <http://ccs.lbl.gov/ITOUGH2>.

The key elements of an inverse modeling code are a simulator such as T2VOC to model flow and transport in the hydrogeologic system ("forward modeling"), the objective function which measures the misfit between the model output and the data, the minimization algorithm which reduces the objective function by automatically updating parameter values, and the error analysis which allows one to judge the quality of the estimates. These elements are shown in Fig. B.1 which summarizes the analyses handled by ITOUGH2. The objective function and minimization algorithm are briefly described below.

Figure B.1 Inverse modeling flow chart. The model in the middle used in VZMS enhanced data analysis is the numerical simulator T2VOC.

B.2 Objective Function

ITOUGH2 estimates elements of a parameter vector $\mathbf{p}$ based on observations summarized in vector $\mathbf{z}^*$ by minimizing an objective function S which is a function of the residual vector $\mathbf{r}$. Vector $\mathbf{p}$ of length n contains the parameters to be estimated by inverse modeling, or the parameters considered uncertain for uncertainty propagation analysis.

$$\text{Parameter vector: } \mathbf{p}^T = [p_1, p_2, \dots, p_n] \quad (\text{B.1})$$

In the simplest case, the parameter p to be estimated is identical with a TOUGH2 input parameter X . For example, p is the porosity of a certain rock type, or a parameter of the capillary pressure function. Other parameters include initial and boundary conditions, or geometrical features such as fracture spacing. ITOUGH2 also allows one to estimate a single parameter which will be assigned to multiple TOUGH2 input variables, i.e., X can represent more than one TOUGH2 variable. Moreover, user-specified parameters can be programmed into ITOUGH2. Simple parameter transformations can be employed to make the inverse problem more linear or to change the distributional assumption about the parameter. For example, the log-normal character of permeability suggests estimating the logarithm of permeability rather than permeability itself. While the transformation does not change the best estimate parameter set, it makes the detection of the corresponding minimum of the objective function more robust.

Vector $\mathbf{z}$ of length m contains dependent, observable variables, usually related to measurements taken at discrete points in space $\mathbf{x}$ and time t . Such a selected point in space and time, $z_i(\mathbf{x}_j, t_k)$, will be referred to as a calibration point. Elements of $\mathbf{z}$ refer to both measured quantities (data), indicated by an asterisk (*), and simulation results. The most commonly used observations for calibration are pressure, flow rate, temperature and concentration measurements.

$$\text{Observation vector: } \mathbf{z}^T = \mathbf{z}(\mathbf{x}_j, t_k)^T = [z_1, \dots, z_n, z_{n+1}, \dots, z_m] \quad (\text{B.2})$$

The vector of observable variables may also contain measured parameter values. For example, if permeability has been measured on cores in the laboratory, this information can be considered as an additional data point, and treated along with the direct observations of the system response. Such measured parameter values are referred to as "prior information". The first n elements of $\mathbf{z}$ are therefore identical to the variables of $\mathbf{p}$.

The residual vector $\mathbf{r}$ contains the differences between the measured and calculated system response; the latter is a function of parameter vector $\mathbf{p}$:

$$\text{Residual vector: } \mathbf{r}^T = (\mathbf{z}^* - \mathbf{z}(\mathbf{p}))^T = [r_1, \dots, r_n, r_{n+1}, \dots, r_m] \quad (\text{B.3})$$

For example, element r_i ($i > n$) is the difference between the measured and calculated pressure at a certain point in space and time. A special type of residual (for $i \leq n$) is the difference between the measured parameter p_i^* (prior information, if available) and the estimated parameter value.

The elements of vectors $\mathbf{z}$ and $\mathbf{r}$ may have different physical meanings with different units of measurement, and represent observations of different accuracy. The inverse of the covariance matrix of $\mathbf{z}$ can be used as a scaling matrix. If taking the view of maximum likelihood estimation, the covariance matrix is part of the stochastic model, i.e., it represents the distributional assumption about the measurement errors. A reasonable assumption about the measurement errors is that they are a result of many individual error sources, and are thus uncorrelated, normally distributed random variables with zero mean.

The objective function S is a measure of the misfit between the data and the model calculation. If the measurement errors $(\mathbf{z}^* - \mathbf{z})$ are normally distributed with mean $E[(\mathbf{z}^* - \mathbf{z})] = \mathbf{0}$ and covariance matrix $E[(\mathbf{z}^* - \mathbf{z})(\mathbf{z}^* - \mathbf{z})^T] = \mathbf{C}_{zz}$, maximum-likelihood theory yields the weighted least-squares objective function:

$$S = (\mathbf{z}^* - \mathbf{z})^T \mathbf{C}_{zz}^{-1} (\mathbf{z}^* - \mathbf{z}) = \mathbf{r}^T \mathbf{C}_{zz}^{-1} \mathbf{r} = \sum_{i=1}^m \frac{r_i^2}{\sigma_i^2} \quad (\text{B.4})$$

Alternative objective functions are available in ITOUGH2 (see Finsterle [1997a]). The best estimate parameter set minimizes the objective function (B.4). Minimization of the objective function S is based on local linearization (see Levenberg-Marquardt algorithm below). The partial derivatives of the calculated system response with respect to the parameters are summarized in the Jacobian matrix $\mathbf{J}$ of dimensions $m \times n$, the elements of which are defined as follows:

$$J_{ij} = -\frac{\partial r_i}{\partial p_j} = \frac{\partial z_i}{\partial p_j} \quad (\text{B.5})$$

ITOUGH2 calculates $\mathbf{J}$ numerically by means of either forward or centered finite differences. The Jacobian is also important in the *a posteriori*, linear error analysis as well as the uncertainty propagation analysis.

B.3 Minimization Algorithm

While ITOUGH2 offers a number of different minimization algorithms, the Levenberg-Marquardt modification of the Gauss-Newton algorithm is found to be a rather general and robust procedure for iteratively updating parameter vector $\mathbf{p}$ (Levenberg, 1944; Marquardt, 1963). It can be described as shown in Table B.1. The Levenberg parameter λ is decreased after each successful step. With decreasing λ , the parameter update $\Delta\mathbf{p}$ converges to the one proposed by the Gauss-Newton algorithm with its quadratic convergence rate.

Table B.1. Levenberg-Marquardt Minimization Algorithm

Step 1: Initialization:

- set iteration index $k = 0$
- define initial Levenberg parameter λ (e.g., $\lambda^{(k=0)} = 10^{-3}$)
- define Marquardt parameter ν (e.g., $\nu = 10$)
- define initial parameter set $\mathbf{p}^{(k=0)} = \mathbf{p}_0$ (e.g., $\mathbf{p}_0 = \mathbf{p}^*$)

Step 2: evaluate $\mathbf{r}(\mathbf{p}^{(k)})$, $S(\mathbf{p}^{(k)})$, and $\mathbf{J}(\mathbf{p}^{(k)})$

Step 3: propose parameter update $\Delta\mathbf{p}$:

$$\Delta\mathbf{p} = \left(\mathbf{J}^T \mathbf{C}_{zz}^{-1} \mathbf{J} + \lambda \mathbf{D} \right)^{-1} \mathbf{J}^T \mathbf{C}_{zz}^{-1} \mathbf{r}$$

where $\mathbf{D} = n \times n$ diagonal matrix with $D_{ii} = \left(\mathbf{J}^T \mathbf{C}_{zz}^{-1} \mathbf{J} \right)_{ii}$

Step 4: - update parameter vector:

$$\mathbf{p}^{(k+1)} = \mathbf{p}^{(k)} + \Delta\mathbf{p}$$

- evaluate $S(\mathbf{p}^{(k+1)})$

Step 5: if $S(\mathbf{p}^{(k+1)}) > S(\mathbf{p}^{(k)})$ increase λ by factor ν and go to Step 3

if $S(\mathbf{p}^{(k+1)}) < S(\mathbf{p}^{(k)})$ decrease λ by factor ν and go to Step 6

Step 6: if no further improvement, stop, else $k = k + 1$ and go to Step 2

B.4 Summary

ITOUGH2 provides extensive inverse modeling, sensitivity, and uncertainty analysis capabilities applicable to T2VOC simulations. More details about inverse modeling theory, objective functions, minimization algorithms, residual and error analysis, as well as extensive sample problems can be found in Finsterle (1997b).

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